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**CHEMISTRY
AND
TECHNOLOGY
OF BASIC
ORGANIC
AND
PETROCHEMICAL
SYNTHESIS**

1



Н.Н.ЛЕБЕДЕВ
ХИМИЯ И ТЕХНОЛОГИЯ
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PREFACE

This is an English version of the textbook published in Russian in 1981 (the third Russian edition). The presentation of the material on basic chemical processes follows the pattern widely adopted in most educational institutions. This has made possible a unified presentation of the theory and technology of the most important processes and provides a better understanding of the methods of manufacture of numerous products of basic and petrochemical synthesis.

Much emphasis is placed on the problems of the economy of raw materials and energy, environmental protection, and on the new trends in the development of the processes.

The author will be grateful for any comments and criticisms.

CONTENTS

Preface	5
Introduction	11
1.1. The Most Important Products of Basic Organic and Petrochemical Synthesis	12
1.2. Development of Basic Organic and Petrochemical Synthesis Technology	20

VOLUME 1

Chapter 1. Starting Materials for Basic Organic and Petrochemical Synthesis	26
1.1. Paraffins	26
1.1.1. Derivation of Lower Paraffins from Natural and Casing-head Gases	27
1.1.2. Derivation of Higher Paraffins from Petroleum Products	31
1.1.3. Isomerization of Paraffins	33
1.2. Olefins	36
1.2.1. Theoretical Foundations of Cracking and Pyrolysis	39
1.2.2. Technology of Cracking and Pyrolysis	46
1.2.3. Derivation and Concentration of Olefins	50
1.2.4. Production of Olefins by Their Interconversion Reactions	60
1.3. Aromatic Hydrocarbons	64
1.3.1. Aromatization of Petroleum Products	65
1.3.2. Coal Coking	71
1.3.3. Derivation and Concentration of Aromatic Hydrocarbons	74
1.3.4. Production of Aromatic Hydrocarbons by Isomerization and Dealkylation	77
1.4. Acetylene	81
1.4.1. Production of Acetylene from Calcium Carbide	83
1.4.2. Production of Acetylene from Hydrocarbons	87
1.4.3. Comparison of Methods of Acetylene Production	92
1.5. Carbon Monoxide and Synthesis Gas	92
1.5.1. Production of Synthesis Gas by Catalytic Conversion of Hydrocarbons	93
1.5.2. Production of Synthesis Gas by High-Temperature Conversion of Hydrocarbons	98
1.5.3. Production of Synthesis Gas by Coal Gasification	100
1.5.4. Production of Concentrated Carbon Monoxide	102

Chapter 2. Halogenation Processes	103
2.1. General Description of Halogenation Processes	103
2.2. Radical-Chain Chlorination	108
2.2.1. Chemistry and Theoretical Foundations of the Process	108
2.2.2. Technology of Liquid-Phase Chlorination	117
2.2.3. Technology of Gas-Phase Chlorination	125
2.3. Ionic-Catalytic Halogenation	130
2.3.1. Additive Halogenation by Free Halogens	130
2.3.2. Hydrohalogenation Processes	137
2.3.3. Nuclear Chlorination of Aromatic Compounds	143
2.3.4. Halogenation of Oxygen-Containing and Nitrogen Compounds	147
2.4. Decomposition Reactions of Chloro Derivatives. Combined and Coupled Chlorination Reactions	153
2.4.1. Decomposition Processes, Their Combination and Coupling with Chlorination Reactions	154
2.4.2. Oxidative Chlorination and Synthesis of Chloro Derivatives Combined with Oxidative Chlorination	161
2.5. Fluorination Processes	168
2.5.1. Fluorination by Molecular Fluorine and Higher Metal Fluorides	169
2.5.2. Fluorination by Hydrogen Fluoride and Its Salts. Production of Fluoro-Olefins	171
 Chapter 3. Hydrolysis, Hydration, Dehydration, Esterification and Amidation	 179
3.1. Hydrolysis and Alkaline Dehydrochlorination of Chloro Derivatives	180
3.1.1. Chemistry and Theoretical Foundations of the Hydrolysis of Chloro Derivatives	181
3.1.2. Production of Chloro-Olefins and α -Oxides by Alkaline Dehydrochlorination	186
3.1.3. Production of Alcohols and Phenols by Hydrolysis	189
3.2. Hydration and Dehydration Processes	193
3.2.1. Chemistry and Theoretical Foundations of the Process	193
3.2.2. Hydration of Olefins and Acetylene	199
3.2.3. Dehydration Processes	209
3.3. Esterification Processes	215
3.3.1. Chemistry and Theoretical Foundations of Esterification Processes	215
3.3.2. Technology of the Synthesis of Esters of Carboxylic Acids	222
3.3.3. Production of Esters from Acid Chlorides. Carbonates and Esters of Phosphorus Acids	230
3.4. Synthesis and Conversions of Nitrogen Derivatives of Acids	234
3.4.1. Synthesis and Conversions of Nitrogen Derivatives of Carboxylic Acids	234
3.4.2. Synthesis and Conversions of Nitrogen Derivatives of Carbonic Acid	243
 Chapter 4. Alkylation Processes	 251
4.1. General Description of Alkylation Reactions	251
4.2. C-Alkylation	256
4.2.1. Chemistry and Theory of the Alkylation of Aromatic Compounds in the Ring	256

4.2.2. Technology of the Alkylation of Aromatic Hydrocarbons	263
4.2.3. Alkylation of Phenols	270
4.2.4. Alkylation of Paraffins	276
4.3. Alkylation at Oxygen, Sulphur and Nitrogen Atoms	281
4.3.1. O-Alkylation	281
4.3.2. S-Alkylation	284
4.3.3. Synthesis of Amines by N-Alkylation Reactions	287
4.4. β -Ethoxylation and Other Syntheses Based on α -Oxides	297
4.4.1. Chemistry and Theoretical Foundations of Syntheses from α -Oxides	297
4.4.2. Technology of Syntheses from α -Oxides	302
4.5. Vinylation Processes	313
4.5.1. Vinylation Catalyzed by Transition-Metal Salts	314
4.5.2. Vinylation Catalyzed by Alkalis	317
4.6. Alkylation at Atoms of Other Elements	320
4.6.1. Synthesis of Organosilicon Compounds	320
4.6.2. Organoaluminium Compounds and Syntheses Based on Them	324

VOLUME 2

Chapter 5. Sulphation, Sulphonation and Nitration Processes	343
5.1. Sulphation of Alcohols and Olefins. Surfactants of the Alkyl Sulphate Type	343
5.2. Sulphonation Processes. Surfactants of the Alkene and Aryl Sulphonate Types	353
5.3. Sulphochlorination and Sulphoxidation of Paraffins. Surfactants of the Alkyl Sulphonate Type	362
5.4. Nitration Processes	369
5.4.1. Nitration of Aromatic Compounds	369
5.4.2. Nitration of Saturated Hydrocarbons	372
Chapter 6. Oxidation Processes	378
6.1. General Description of Oxidation Processes	379
6.2. Homogeneous Oxidation at the Saturated Carbon Atom	384
6.2.1. Scientific and Engineering Foundations of the Process	385
6.2.2. Oxidation of Hydrocarbons to Hydroperoxides. Production of Phenol and Acetone	397
6.2.3. Oxidation of Paraffins	407
6.2.4. Oxidation of Naphthenes and Their Derivatives	415
6.2.5. Oxidation of Methylbenzenes to Aromatic Acids	425
6.2.6. Oxidation of Saturated Aldehydes and Alcohols	434
6.3. Heterogeneous-Catalytic Oxidation of Hydrocarbons and Their Derivatives	441
6.3.1. Scientific and Engineering Foundations of the Process	442
6.3.2. Oxidation of Olefins at the Saturated Carbon Atom	449
6.3.3. Oxidative Ammonolysis of Hydrocarbons	453
6.3.4. Production of Phthalic, Maleic and Other Cyclic Anhydrides	459
6.3.5. Production of Ethylene Oxide	464
6.4. Oxidation of Olefins Catalyzed by Metal Complexes	469
6.4.1. Epoxidation of Unsaturated Compounds	470
6.4.2. Oxidation and Oxidative Coupling of Olefins Catalyzed by Metal Complexes	479

Chapter 7. Dehydrogenation and Hydrogenation Processes	488
7.1. Physicochemical Foundations of Dehydrogenation and Hydrogenation Processes	492
7.1.1. Thermodynamics of Dehydrogenation and Hydrogenation Reactions	492
7.1.2. Catalysis, Mechanism and Kinetics of Dehydrogenation and Hydrogenation Reactions	498
7.2. Chemistry and Technology of Dehydrogenation Processes	505
7.2.1. Dehydrogenation and Oxidation of Alcohols	505
7.2.2. Dehydrogenation of Alkylaromatic Compounds. Production of Styrene and Its Homologues	511
7.2.3. Dehydrogenation of Paraffins and Olefins. Production of Butadiene and Isoprene	516
7.3. Chemistry and Technology of Hydrogenation Processes	530
7.3.1. Hydrogenation of Hydrocarbons	530
7.3.2. Hydrogenation of Oxygen-Containing Compounds	535
7.3.3. Hydrogenation of Nitrogen Compounds	544
7.3.4. Technology of Liquid-Phase Hydrogenation	550
7.3.5. Technology of Gas-Phase Hydrogenation	556
 Chapter 8. Syntheses Based on Carbon Monoxide	 561
8.1. Syntheses from Carbon Monoxide and Hydrogen	561
8.2. Oxo Synthesis	568
8.3. Synthesis of Carboxylic Acids and Their Derivatives Based on Carbon Monoxide	579
 Chapter 9. Condensation at the Carbonyl Group	 584
9.1. Condensation of Aldehydes and Ketones with Aromatic Compounds	586
9.2. Synthesis of Acetals and the Prins Reaction. Production of Isoprene	592
9.3. Condensation of Aldehydes and Ketones with Nitrogen Bases. Production of Caprolactam	598
9.4. Reactions of the Aldol Condensation Type	611
 Subject Index	 628

INTRODUCTION

The production of organic substances was started long ago, but originally it was based on the processing of vegetable and animal materials which consisted of the derivation of valuable substances (sugar, butter) or of their decomposition (soap, alcohol, etc.). Organic synthesis, i.e., the production of more complex substances from comparatively simple ones, originated in the middle of the 19th century on the basis of the coal coking by-products composed of aromatic compounds. Later, in the 20th century crude oil and natural gas became increasingly important as sources of organic raw materials because their production, transportation and processing were more economical than in the case of coal. The organic synthesis industry today is based on these three types of raw materials. The processes involving their physical separation, thermal or catalytic decomposition (coking, cracking, pyrolysis, reforming, conversion) yield five principal groups of starting compounds for the synthesis of many thousands of other compounds:

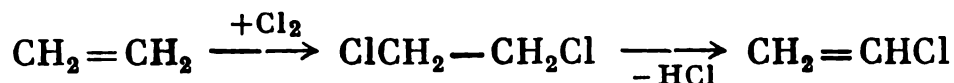
- (1) paraffinic hydrocarbons (from CH_4 to $\text{C}_{15}\text{-C}_{40}$);
- (2) olefins or alkenes (C_2H_4 , C_3H_6 , C_4H_8 , C_5H_{10});
- (3) aromatic hydrocarbons (benzene, toluene, xylenes, naphthalene);
- (4) acetylene;
- (5) carbon monoxide and synthesis gas (a mixture of CO and H_2).

During its development the organic synthesis industry has been split into a number of branches (dye industry, drug industry, plastics technology, chemical fibre production, etc.), among which an important role is played by the industry of basic organic and petrochemical synthesis. The term "basic" organic synthesis embraces the production of multitonnage products, which serve as the basis for the rest organic chemical industry. The term "petrochemical" synthesis was coined in connection with the switch of the organic chemicals industry to petroleum chemicals, and in the ordinary sense of the term (excluding the production of inorganic substances and polymers) it covers the primary chemical processing of hydrocarbons of petroleum origin. In this sense, it is a part of basic organic synthesis, which is why the terms are combined.

I.1. The Most Important Products of Basic Organic and Petrochemical Synthesis

The products of this branch of industry differ widely in structure, properties and areas of application. They include various hydrocarbons, chlorine and fluorine derivatives, alcohols and phenols, ethers, aldehydes and ketones, carboxylic acids and their derivatives (esters, anhydrides, nitriles, etc.), amines and nitro compounds, sulphur- and phosphorus-containing compounds, and so on. According to their application, all these products are divided into two groups: (1) intermediate products for the synthesis of other substances in this or other branches of organic chemical production; (2) products for specialized applications in various sections of national economy.

Intermediate Products. Many compounds, which find no application in national economy, are mainly used as sources for the synthesis of other valuable compounds. These are intermediate products of organic synthesis. For example, the bulk quantity of 1,2-dichloroethane is used for the production of vinyl chloride:

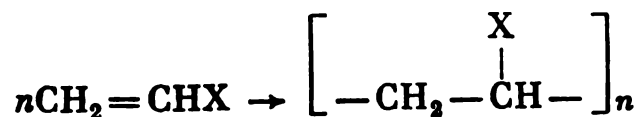


The same refers to many other chlorine derivatives, aldehydes, olefin oxides, etc.

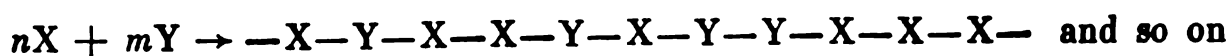
The role, scale of production and range of intermediate products are enormous, since the synthesis of even comparatively simple and complex organic compounds from paraffins, olefins, etc., involves a number of intermediate steps.

Monomers and Starting Compounds for Polymeric Materials. The production of these materials plays a most important role in basic organic and petrochemical synthesis, which supplies raw materials for the manufacture of plastics, synthetic rubber, synthetic varnishes, glues, film materials, fibres, etc.

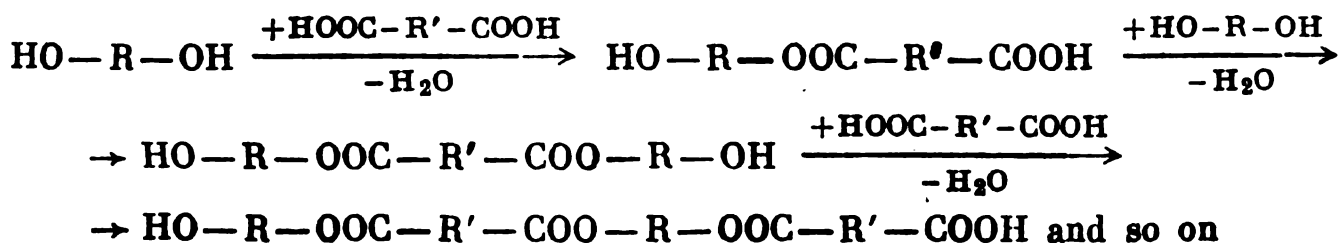
All synthetic polymers are produced by two main processes—polymerization and polycondensation. The first of these reactions requires monomers, i.e., substances capable of combining under the influence of heat, light, radiation or catalysts (with no low-molecular-weight compounds formed) into long chains of a polymer having the same composition of repeating units as in the starting monomer:



The copolymerization of two or more different monomers yields polymers, whose macromolecules are built of monomeric units, which recur in various ways:

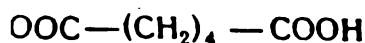


Polycondensation reactions usually take place through the elimination of a low-molecular-weight component (H_2O , HCl , etc.) and the polymers produced differ in composition from the reactants used. In this case, it would be more correct to use, instead of monomers, the term starting compounds or reactants for the synthesis of polycondensation polymers. For a macromolecule to grow continuously it is required that the starting compounds contain, at least, two functional groups capable of reacting with each other. For instance, the process leading to the formation of polyesters involves the interaction of hydroxyl and carboxyl groups:

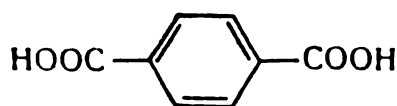


The most important among the polymerizable monomers are compounds with a double carbon-carbon bond. Examples are monoalkenes (ethylene, propylene, isobutylene), dienes (1,3-butadiene and isoprene, which are the main starting compounds for the production of rubber) and styrene. Of importance are also vinyl and various halogen-containing monomers: vinyl acetate ($\text{CH}_2=\text{CH}-\text{OCOCH}_3$), vinyl chloride ($\text{CH}_2=\text{CHCl}$), and acrylic monomers, in which the double bond is present in the acid residue [for example, acrylonitrile, $\text{CH}_2=\text{CHCN}$, and methyl methacrylate, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$].

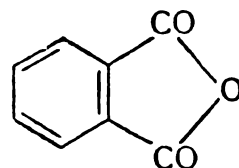
The starting compounds used for polycondensations are various di- and polyfunctional compounds. These are dicarboxylic acids, their anhydrides and acid chlorides:



Adipic acid

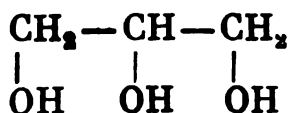


Terephthalic acid



Phthalic anhydride

phosgene, COCl_2 , and also a number of polycarboxylic acids and their acid anhydrides, glycols and polyglycols, diamines:



Glycerol



Pentaerythritol



Hexamethylene diamine

Phenol, formaldehyde, melamine, their homologues and analogues have become very important in the production of phenol-aldehyde and carbamide- and melamine-formaldehyde polymers. A number of dichloro derivatives, $\text{Cl}-(\text{CH}_2)_n-\text{Cl}$, organosilicon compounds,

R_2SiCl_2 , and diisocyanates, $O=C=NRN=C=O$, are used for the manufacture of polysulphides, silicone polymers, polyurethanes, etc.

The purity of the reactants is very important in polymerization and polycondensation reactions. The impurities can inhibit the reaction or terminate the growth of the molecule during the polymerization, and upset the required ratio of starting compounds in polycondensations, etc., leading to polymers with a too small molecular mass and low technical indices. In this respect, very high requirements are set forth to the products of basic organic and petrochemical synthesis; the purity of monomers not infrequently must correspond to the 99.8-99.9-percent content of the main substance.

Plasticizers and Other Additives for Polymeric Materials. Apart from monomers and starting compounds, the production of synthetic polymers requires the use of plasticizers and other additives, which facilitate the synthesis or improve the technical properties of polymers and polymeric articles.

Plasticizers are substances which are added to some polymers in an amount of 30-40 percent to improve the flow properties of the materials and to increase their softness and flexibility. This is required, first of all, in the processing of polymers by compression moulding, calendering and by other methods, for which purpose they must be sufficiently fluid and, second, during the use of the articles, which must be sufficiently elastic, must not crack in storage and service, etc. The prime requisites for a plasticizer are good compatibility with the polymeric material and low volatility, which determine the quality of the articles and their service life without loss of plasticizer.

One of the most important groups of plasticizers are high-boiling esters, say dibutyl and dioctyl phthalates, tricresyl phosphate, some esters of higher alcohols with dicarboxylic acids or esters of higher carboxylic acids with dihydric alcohols. Apart from mineral oils, the plasticizers used for synthetic rubbers include synthetic products—alkyl-aromatic hydrocarbons, lower polyolefins, etc.

The industry of basic organic and petrochemical synthesis also produces other additives used in polymer technology, namely, promoters and catalysts, which speed up the polymerization process; modifiers and inhibitors, which limit the growth of the chain or hinder polymerization; stabilizers which protect plastic from the degradation by heat and light, etc.

Synthetic Surface-Active Substances (Surfactants) and Detergents. Surface-active properties appear in organic compounds, whose molecules contain a hydrophobic group which is soluble in oil but not in water, and a hydrophilic (polar) group which is water-soluble but insoluble in oil. In ordinary soap—the sodium salt of stearic or palmitic acid, $R-COONa$, the hydrophobic group is the long

hydrocarbon chain and the hydrophilic group is the carboxylate ions.

Owing to this specific structure, surface-active substances concentrate at the water-oil interface, their hydrophobic groups being attracted to the oil and the hydrophilic groups to the water. As a result, the surface tension of the latter is considerably lowered with the result that a soap solution wets a fabric much more readily than pure water and the oil remains suspended as a colloid. Surfactants also display emulsifying and dispersing properties, foam-forming ability, etc.

Surface-active substances and detergents (cleansing agents) are especially widely used in the home, for the washing of textiles and articles and for cleansing various things. In the textile industry, they are employed for the treatment of fabrics prior to dyeing, for the washing of wool and fibres; in machine-building and metal-working industries they are used for metal cutting, for the cleansing of machine parts from oils and mechanical contaminants; in the perfume industry they find application as a component of toilet soap and cosmetics. In chemical technology, surfactants and detergents serve as emulsifiers in heterophase reactions (especially in emulsion polymerization), for the preparation of stable pesticide emulsions used in the home and agriculture. Surfactants find an ever increasing use in ore flotation, in the production of foamed concrete and other construction materials, in the petroleum industry, where the use of surfactants enables the output of an oil deposit to be increased considerably, and so on.

Surface-active substances and detergents are classified into *ionic* and *non-ionic*, which mean the presence or absence of groups capable of dissociation in aqueous solutions. There are two types of ionic detergents: anionic and cationic, whose surface-active properties are determined, respectively, by the anion or cation formed upon dissociation.

Anionic detergents are the most important industrial detergents, including soap, either ordinary soap or soap produced from synthetic fatty acids (the active part of the molecule is the RCOO^- group). Such surfactants give alkaline reaction and destroy the fabrics; they form insoluble salts with magnesium and calcium salts with the result that their detergent properties in hard water are reduced; they display activity only at a considerable concentration in water. These shortcomings are absent in most modern synthetic anion-active substances, which are largely the sodium salts of organic sulphonic acids and of acid esters of sulphuric acid (alkyl hydrogen sulphates). They include alkylaryl sulphonates, $\text{RC}_6\text{H}_4\text{SO}_2\text{ONa}$, alkyl sulphonates, RSO_2ONa , and alkyl sulphates, ROSO_2ONa , with alkyl $\text{C}_{12}\text{-C}_{18}$ groups.

Cationic detergents are comparatively of little importance. They

are mostly the salts of amines or quaternary ammonium bases, say the salt of alkylbenzyltrimethylammonium, $[\text{RC}_6\text{H}_4\text{CH}_2\text{N}(\text{CH}_3)_3]^+\text{Cl}^-$.

Non-ionic detergents have recently found an ever increasing application. They are synthesized from ethylene oxide and various organic substances—carboxylic acids, alcohols, amines and other compounds with active hydrogen atoms. Hydrophilic properties are conferred on them by the polyoxyethylene chain, such as, for example, $\text{R}(\text{OCH}_2-\text{CH}_2)_n\text{OH}$.

In order to improve detergent properties and to reduce its consumption, a surfactant is mixed with various additives. Detergents (say, those for use in automatic washers) have the following components: sodium phosphate, pyrophosphate or hexametaphosphate, silicate, sodium sulphate and carbonate, perborates, carboxymethyl cellulose ($\text{Cell.}-\text{O}-\text{CH}_2-\text{COONa}$). Some of them are added to produce a weakly alkaline medium or to improve the colloid structure of the solution; others serve as bleaching agents or prevent the re-deposition of the detached dirt onto the fabric.

Since surface-active substances are disposed into sewage after being used up, an important requirement is high degree of their biodegradability, i.e., the ability to be oxidized to harmless substances by the action of microorganisms present in natural water basins. This imposes certain limitations on the structure of the hydrocarbon residue, which must not be branched.

Synthetic Fuels, Lubricating Oils and Additives. Many products of basic organic and petrochemical synthesis are important in automobile transport, aircraft, rocket engineering, etc. They include synthetic motor and jet fuels, lubricating oils, additives which improve the properties of fuels and oils, antifreezes which prevent the freezing of cooling liquids, and braking and hydraulic fluids.

Organic synthesis solved the problem of the preparation of hydrocarbons from CO and H_2 , which enabled the production of a liquid fuel from coal. Later, internal-combustion engines required a high-octane fuel, and isoparaffins were synthesized, notably isooctane, $(\text{CH}_3)_2\text{CH}-\text{CH}_2-\text{C}(\text{CH}_3)_3$, which is the reference fuel (100 octane number); more correctly it is 2,2,4-trimethylpentane. The high-octane components used for motor fuels are isopropyl benzene, $\text{C}_6\text{H}_5-\text{CH}(\text{CH}_3)_2$, methyl alcohol, *tert*-butylmethyl ether, $(\text{CH}_3)_3\text{C}-\text{O}-\text{CH}_3$, etc. Methanol and *tert*-butylmethyl ether have recently become promising.

Synthetic fuels have recently found a new area of application—rocket engineering. In liquid-fuel rocket systems use is made of synthetic fuels (methanol, ethanol, ethylamines, dimethyl hydrazine, some organometallic compounds), which have substantial advantages over hydrocarbons.

Lubricating oils are still largely produced from petroleum, but the development of new techniques imposes ever increasing require-

nents which cannot be met by mineral oils. The operation of engines over a wide temperature range (from -60 to 300°C upwards), the possibility of their starting at a low temperature, high loads at a large number of revolutions, etc., required the production of synthetic lubricating oils. They must be low-volatile, cause no corrosion of metals, must not congeal at low temperatures, and must be sufficiently resistant to oxidation and thermal decomposition. A valuable property of lubricating oils is that their viscosity depends little on temperature. Lubricating oils intended for specialized applications must have high thermal stability and be capable of long performance at $300-400^{\circ}\text{C}$.

Synthetic lubricating oils belong to several groups of organic compounds, among which the most important are the following: synthetic hydrocarbons (lower polymers of olefins and alkylated aromatic hydrocarbons); esters of dicarboxylic acids with higher monohydric alcohols and esters of higher monocarboxylic acids with polyhydric alcohols; high-boiling fluorocarbons and fluorochlorocarbons (in these compounds the hydrogen atoms are completely replaced by a halogen); organosilicon polymers with a siloxane bond, $\text{Si}-\text{O}-\text{Si}$.

Various additives that improve the performance of fuels and oils and their stability on storage have become increasingly important. Antioxidants for fuels and lubricating oils and also for polymers (for example, alkylated phenols) slow down autoxidation chain reactions. There are also additives which increase the fluidity of oils at low temperatures (pour-point depressants), improve their viscous properties (viscosity-index improvers), prevent the corrosion of metals (corrosion inhibitors), etc. Mention should also be made of the well-known antiknock additive—tetraethyllead, which considerably increases the octane number of motor fuels.

Solvents and Extractants. Until recently the choice of solvents and extracting agents has been rather limited, including mainly petrol (gasoline), benzene, and ethyl alcohol (ethanol). The development of the industry and national economy required substances having various specific solvent and extracting abilities with respect to various classes of compounds. Synthetic solvents must also be cheap, easily available and little toxic. Their boiling temperature must not be too low in order to avoid considerable losses and too high to be regenerated by distillation. In a number of cases, solvents have been synthesized which have low flammability and are even noncombustible.

Today, solvents and extractants are extensively used for the derivation of aromatic hydrocarbons from petroleum products, in the processes of azeotropic and extractive distillation, for the extraction of fats and oils from natural substances. In the chemical industry, they are often used for purification and recrystallization, as

absorbents for gases and vapours (for example, for acetylene and volatile substances entrained by gases), and for the synthesis of polymers (especially in the paint-and-varnish industry), etc.

In the machine-building and metal-working industries, solvents are used to degrease and clean machine parts. In agriculture, solvents are needed when pesticides are used. Complex-forming extractants are used to separate compounds of uranium, rare and scattered elements from ores.

Synthetic solvents and extractants may belong to various groups of organic compounds. These include chlorine derivatives of hydrocarbons (carbon tetrachloride, methylene chloride, tri- and tetrachloroethylene), alcohols (ethanol, propanol, butanol, pentanol), cello-solves, ethers (diethyl ether, diisopropyl ether, and higher ethers), ketones (acetone, methyl ethyl ketone, isobutyl methyl ketone), esters (ethyl, butyl and amyl acetates) and also dimethylformamide, $\text{HCON}(\text{CH}_3)_2$, dimethyl sulphoxide, $(\text{CH}_3)_2\text{S}=\text{O}$, and others.

Pesticides and Chemical Means of Plant Protection. Pesticides are toxic chemicals used against diverse living organisms, ranging from bacteria and fungi to weeds and rodents and other specified animals. The major proportion of pesticides is used in agriculture as chemical means of plant protection; moreover, they are used in the home, for the control of certain diseases and epidemics, for the elimination of pests in storage places, in the holds of ships, in apartment buildings, etc. The use of pesticides in agriculture enables the prevention of many diseases of field and garden crops and considerably reduces harvest losses. In view of this, the chemical means of vegetable protection have become as important a factor as chemical fertilizers in raising harvest.

There are several groups of pesticides which have specific effects on various living organisms.

Fungicides and *bactericides* are active towards the lowest organisms, fungi and bacteria, respectively. In agriculture, they are used to combat various diseases of growing crops. Bactericides that are harmless to man are used in the canned food industry, and others (say, pentachlorophenol) for the preservation of wood, in medicine, etc.

Insecticides are among the most important pesticides; they are used to kill insects and their larvae. In contrast to insecticides, *repellents* only serve to repel insects—mosquitoes, blood-sucking flies, etc.

An important group of pesticides includes *herbicides* and *defoliants* which have an effect on plants. Herbicides are used as weed-killers, and defoliants for defoliating plants as an aid to mechanical harvesting.

Rodenticides are commonly classified as lethal chemical agents used to kill warm-blooded pests—rodents (mice, rats, pouched marmots).

A very important requirement set forth to most pesticides is strict selectivity of their action. For example, herbicides that kill weeds must not affect useful plants. All toxic chemicals used to protect plants must be harmless to man, animals and birds. A valuable property of these chemical control agents is their ability to break down slowly under natural conditions into harmless compounds.

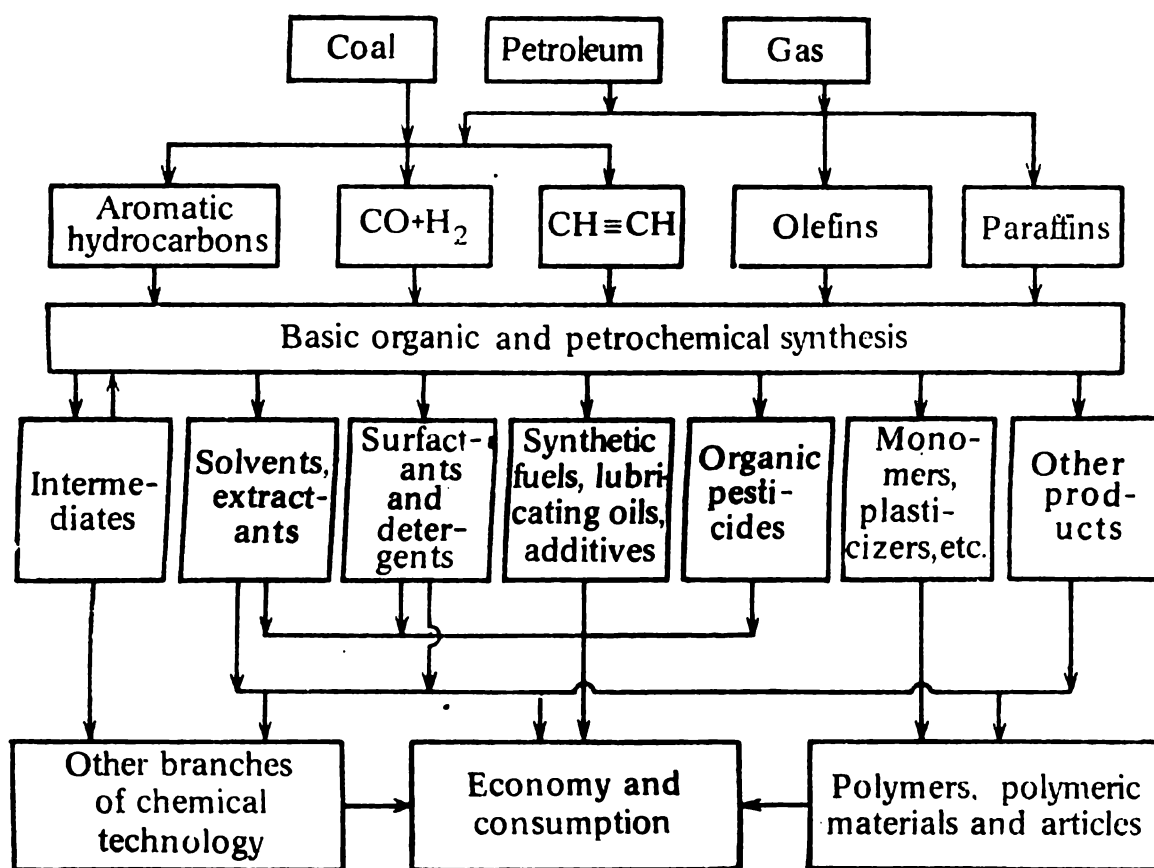


Fig. I.1. The place and role of the industry of basic organic and petrochemical synthesis among other branches of chemical engineering and in national economy.

Organic compounds of many classes are used as pesticidal chemicals: chlorine derivatives, nitrogen- and sulphur-containing compounds, derivatives of acids of phosphorus, etc. The nomenclature and scale of production of pesticides are continuously increased. This is accounted for by the discovery of new, more efficient and selective or less toxic preparations and also by the necessity to carry on a constant combat against nature, which is capable of developing immunity towards chemicals used for a prolonged period of time. Utmost care must however be exercised in the choice and application of pesticides, since they may have aftereffects and upset the balance between various organisms existing in nature.

Thus, basic organic and petrochemical synthesis while being supplied with raw materials by the coal-coking and petroleum-refining industries provides with synthetic products all other branches of organic technology and, besides, yield a number of special-purpose products for the national economy. The place and role of this branch of technology are illustrated in Fig. I.1.

I.2. Development of Basic Organic and Petrochemical Synthesis Technology

This branch of chemical industry began to play an important role in national economy in this country only in the fifties, but it still substantially lagged behind as compared with the level and rate of development in the most advanced capitalist countries. A strong impetus to its advancement was given by the Plenary Session of the Central Committee of the USSR Communist Party held in May, 1958. This Session laid down the task of intensive development of the industry of synthetic materials and of fuller satisfaction of growing demands for these materials. New enterprises were built and the existing ones were expanded; new research and designing institutes were created, and the scope of production and the range of products considerably increased. New advances were made during the years of the Ninth and Tenth Five-Year Plans.

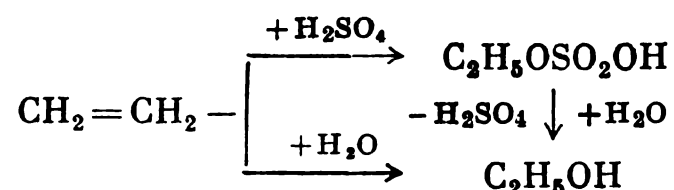
At present the industry of basic organic and petrochemical synthesis in this country is a powerful branch concentrated mainly in large chemical and petrochemical combination plants. Its distinctive features are the enormous variety of the products, reactions employed for their synthesis and processes for the separation of the compounds produced. A large scope of production has become possible due to the extensive use of updated continuous and automated technological processes equipped with diverse high-capacity plants. The range of new products constantly increases, new reactions and catalytic systems are being constantly realized industrially, new equipment is used, etc. An ever increasing use is made of modern methods of mathematical modelling and optimization, automated research work, designing, and production management.

A number of trends appear, which predetermine paths for the development of new industries and improvement of the existing ones. The major trends are associated with the increase of the economic efficiency of production, quality of raw materials and products and with environmental protection. The first of these factors is determined by expenditure on raw materials and energy and by capital investment, the economy of which is part of the solution of the general problem of preservation of natural and energy resources.

The economy of raw materials is the principal driving force in the development of technology, since the cost of raw materials is 50-70 percent of the product cost. This problem is solved along three main directions.

1. *Development of new processes* based on more available or cheaper raw materials is usually the result of the discovery of new reactions and not infrequently has a revolutionizing impact on technological advancement. As regards minerals, this consists of the above-mentioned switch of basic organic synthesis from coal to petroleum and

natural gas. The gradual depletion of oil and gas deposits will sooner or later lead to the use of solid fuel, which will have a strong influence on the entire technology. As far as the five principal groups of starting compounds for organic synthesis are concerned, there has lately been observed the tendency to replace costly acetylene, by lower olefins and even paraffins and also the intensive development of CO- and H₂-based syntheses using coal. In other cases, new processes are being developed with replacement of the raw material: alcohols by olefins; phosgene by carbon dioxide; costly oxidizing agents (bichromate, hydrogen peroxide, nitric acid) by oxygen and air; various reducing agents by hydrogen, etc. This problem also includes the development of direct methods of synthesis, which exclude the consumption of acids or alkalies, say the direct hydration of olefins instead of the sulphuric-acid hydration in the synthesis of alcohols:



2. *Increasing the selectivity* of processes taking place in the chemical reactor is another route to the economy of raw materials. The selectivity is the fraction of the converted reactant used up for the formation of the end product:

$$S_B = \frac{\nu_B}{\nu_A} \cdot \frac{F_B}{F_{A,0} X_A}$$

Here F_B is the molar stream (the number of moles per unit time) of the end product at the reactor outlet; $F_{A,0}$ is the molar stream at the reactor inlet; X_A is the degree of conversion of the reactant; ν_A and ν_B are the stoichiometric coefficients of the overall reaction leading to the formation of product B from reactant A. Obviously, the remainder of the feedstock is used for the formation of by-products.

An increase in selectivity is achieved by an appropriate choice of the process parameters (temperature, pressure, contact time), of the reactor type, more selective catalysts, etc., and is a part of the more general problem of process optimization. An increase in selectivity by even 1 percent means an economy of hundreds of thousands of rubles for a multitonnage production.

3. *Reduction of the losses of raw materials and products* through the apparatus and manifolds, and with effluent gases, sewage and wastes leads to an increase in the yield of the end product:

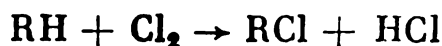
$$y_B = S_B (1 - \eta)$$

Here η is the fraction of various losses. A reduction in the losses is achieved by improving the production and by recovering the raw materials and products from the off-gases and liquid wastes. This

also includes the utilization of by-products and coproducts. By-products are the products of side reactions, say ether in the synthesis of alcohol:



Coproducts are products which are unavoidably produced together with a major product, say HCl in the production of chlorine derivatives:



As a result of their utilization, the fraction of the raw material used up efficiently is increased and the cost of the end product is lowered.

The economy of energy (liquid or gaseous fuels, steam, cooling agents, electric power) is also important, since the expenditure on energy is not infrequently 20-30 percent and more of the product cost. The efficiency of the use of energy is usually estimated from the energy (in this particular case, heat) efficiency of reaction units or plants:

$$\text{Energy efficiency} = \frac{\text{Theoretically required energy}}{\text{Actual energy consumption}} 100\%$$

This quantity, however, takes into account only the amount of energy and not its potential or capacity to do work, which depends on the parameters of steam or cooling agent. Therefore, a more correct estimate is given by the exergy efficiency:

$$\text{Exergy efficiency} = \frac{\text{Theoretically required exergy}}{\text{Actual exergy consumption}} 100\%$$

where the exergy is a function of the difference between the heat content and the entropy of the system in the actual state and under environmental conditions (with the zero index):

$$e = i - i_0 - T_0 (S - S_0)$$

The problems of energy economy and exergy improvement become increasingly important for the further development of technology and are solved in various ways. For example, the heat of hot or cold streams is used for heating or cooling; the heat of exothermic reactions or of heated gases is employed for steam generation; the pressure that results from compression is used for performing useful work or for partial separation of the compounds; use is made of the heat-pump principle, etc. A new approach has been developed for the solution of the problem with the tendency to transform a chemical production into a unified energy-technological system and to use as completely as possible the secondary energy resources. In spite of the growth in capital investment, an ever increasing use is made of stepwise heating or cooling by means of suitable heat-exchange media, of the successive generation of high-, moderate- and low-

pressure steam; this steam is employed not only for heating but also as a working medium for driving turbocompressors or steam pumps. The utilization of heat having lower parameters is in order for producing hot water, for heating the premises, etc.

Economy of capital investments has a bearing on production indices, such as the capital productivity, the time of return on investment, reduced expenditure, etc. It should be noted that many of the measures taken for the saving of raw materials and energy, environmental protection and improvement of the product quality lead to the growth of capital cost. At the same time, the reduction in capital cost is favoured by the absence of corrosive media (due to the use of cheaper steel), a moderate increase of pressure in gas-phase reactions (which leads to a reduction in the volume of the process vessels and manifolds), the simplification of reactor design and especially the intensification of reactions and separation processes.

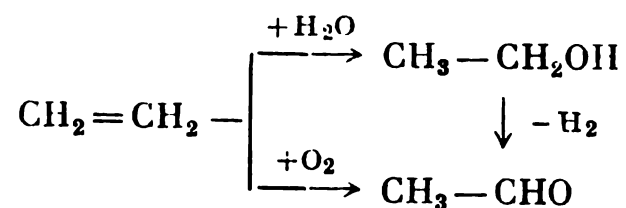
The last-named factor is characterized by the specific capacity (rate of production) which is defined as the amount of product (throughput) per unit volume of the reaction vessel in unit time:

$$G_B = \frac{F_B}{V}$$

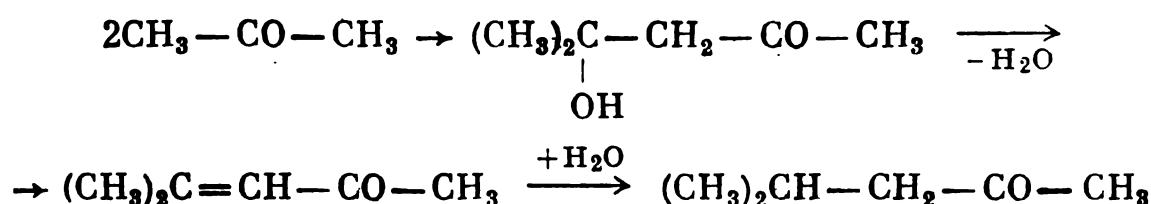
Process intensification is achieved by raising the temperature and pressure, by realizing the appropriate hydrodynamic and thermal regimes, by the choice of active catalysts, etc.

As a result of the process intensification and the increase in the volume of reaction vessels, there is a distinct tendency to increase the unit capacity of equipment, which results in a decrease in specific capital investment. While formerly a capacity of 10,000 to 20,000 tons of product per year was satisfactory, today combination plants are being designed with a unit capacity of 100,000 to 200,000 tons and more per year. This eliminates the need for emergency process lines, vessels and equipment but requires a perfect organization of operations and a sharp increase in the reliability of the equipment.

A decrease in capital cost is also achieved by the development of new processes involving a lesser number of intermediate steps or even single-step processes if this does not lower the other production indices. For example, acetaldehyde was formerly produced from ethylene by carrying out a two-step process (through the intermediate formation of ethanol); today this process has been superseded by the single-step oxidation of ethylene:



Single-step reactions are also possible in coupled processes, where two or more reactions leading to the end product take place in a single apparatus; an example is the production of isobutyl methyl ketone from acetone:



The operation of plants of large unit-capacity and of processes involving a small number of steps leads to a reduction in manpower, to better prerequisites for savings in raw materials and energy.

Environmental protection becomes an increasingly important criterion in the estimation of production and determines the technological development in many respects. One trend is to restrict or prohibit the production of compounds that have a harmful effect on nature or on man (say, many toxic pesticides, bionondegradable surfactants). Another trend is a sharp reduction or complete elimination of toxic wastes disposed into the environment through the above-mentioned utilization of by-products and coproducts for useful purposes and by lowering the losses.

The effluent gases are first processed to recover the entrained volatile compounds, which are then purified from harmful impurities and occasionally burned in special furnaces. Valuable compounds are also recovered from waste waters, which are then freed from toxic impurities by evaporation, extraction, adsorption, oxidation, microbiological purification. Liquid or solid organic wastes are burned in furnaces, as a result of which steam of varying parameters is generated. These operations were also used in the past, but the present-day tendency is to realize a unified system of measures that exclude the disposal of harmful substances into the environment in amounts that exceed the sanitary permissible levels; such a system is called wasteless technology. In order to preserve water resources, wasteless technology is sometimes supplemented by a closed water circuit system, in which the process and waste waters are subjected to appropriate treatment and purification and returned to the process line.

In spite of the extra energy and capital cost, the development and operation of purification units is economically justified in the national economy as a whole; moreover, this leads to the solution of the general problem of environmental protection, which is of great social importance.

The quality of raw materials and products depends on the amount of impurities present, which may be divided into two groups: harmful and inert. The first group includes substances that cause the

corrosion of vessels (HCl , SO_2 , H_2S) and deactivate catalysts (organic sulphur compounds, water) and also initiators that react with the feedstock and form by-products or cause undesirable phenomena during storage or use of the product. Inert impurities are substances which do not cause such effects (for example, ethane present as an impurity in ethylene in many syntheses), but their role may become critical in circulation systems: they are gradually accumulated, thereby causing a decrease in the reaction rate, extra energy consumption, etc.

Evidently, the purity requirements for raw materials and products differ with respect to the impurities of the first and second groups. The harmful impurities are removed as thoroughly as possible, to the extent of their content of 0.001 percent (by weight) and less, whereas the permissible content of inert impurities may be considerably higher. The general tendency is to increase the purity requirements, but there are certain limits that follow from economic considerations. Indeed, the higher the quality of the product, the greater the expenditure on its purification, which must be compared in each particular case with the economic advantages gained by the use of purer raw materials and products.

In the evaluation of the quality of the product an important role is also played by its value as a surfactant, pesticide, etc., which is determined by the increasing demands of present-day engineering, national economy and consumption. New technically important compounds are being sought for; in these searches one is guided by the relationships between the structure and properties of organic compounds.

The tendencies described above manifest themselves differently in the production of raw materials for organic synthesis and in various refining operations. These tendencies have resulted from the scientific-technical revolution, which has also had an impact on the industry of basic organic and petrochemical synthesis.

CHAPTER 1

STARTING MATERIALS FOR BASIC ORGANIC AND PETROCHEMICAL SYNTHESIS

1.1. Paraffins

Saturated hydrocarbons called alkanes, paraffins or paraffinic hydrocarbons, which are technically important for organic synthesis, may be divided into the following groups: lower paraffins (from C_1 to C_5) produced individually and higher paraffins (approximately from C_{10} to C_{40}), which are usually liquid or solid mixtures of homologues with different numbers of carbon atoms.

The Lower Paraffins. The paraffinic hydrocarbons ranging from methane, CH_4 , to butanes, C_4H_{10} , are gaseous substances under ordinary conditions; pentanes, C_5H_{12} , are low-boiling liquids. Their properties are given in Table 1.1. Methane is a difficultly liquefiable gas, and the other gaseous paraffins undergo condensation even when cooled by water under pressure. It is important that the difference in boiling point between butane and isobutane and also between *n*-pentane and isopentane is sufficiently large, which enables the isomers to be separated by fractional distillation.

TABLE 1.1. The Properties of Lower Paraffins

Paraffin	Formula	Condensation point (or boiling point) at atmospheric pressure, °C	Critical temperature, °C	Critical pressure, MPa	Explosive concentration limits in mixture with air, percent by volume
Methane	CH_4	-161.6	-82.1	4.49	5.0-15.0
Ethane	CH_3-CH_3	-88.6	32.3	4.72	2.9-15.0
Propane	$CH_3-CH_2-CH_3$	-42.1	96.8	4.12	2.1-9.5
<i>n</i> -Butane	$CH_3-CH_2-CH_2-CH_3$	-0.5	152.0	3.50	1.8-9.1
Isobutane	$CH_3-CH-CH_3$	-11.7	134.5	3.58	1.8-8.4
	 CH_3				
Isopentane	$CH_3-CH-CH_2-CH_3$	27.8	—	—	1.3-7.6
	 CH_3				

The lower members of the paraffin series dissolve difficultly in water and in polar liquids (in lower alcohols, ketones, aldehydes, etc.) but are absorbed by other hydrocarbons and solid adsorbents

activated charcoal). Their sorption ability increases with increasing molecular mass of the paraffin, a fact which is used to separate the C_3 , C_4 , C_1 and C_2 paraffins by absorption and adsorption.

The lower paraffins form explosive mixtures with air, which is why the departments where these hydrocarbons are produced or used are classified as belonging to the A category. The toxicity of the lower paraffins is not high as compared with other organic compounds, but it cannot be neglected: during constant work, as a result of the inhalation of the gases or vapours, there may gradually be developed narcotic effects with severe consequences.

Of the lower paraffins, methane, *n*-butane and isobutane are most frequently used as raw materials for organic synthesis. Isopentane, methane and especially propane are used much less frequently.

The Higher Paraffins. Only the higher members of the paraffin series containing a straight chain of carbon atoms are mainly of practical value as raw materials for organic synthesis. The individual members up to C_{16} are liquids at room temperature and those higher than C_{16} are solids, whose boiling point increases gradually with increasing carbon chain. The melting points of *n*-paraffins are usually higher than those of the corresponding branched-chain isomers and they crystallize on cooling. Another distinctive feature of normal paraffins is their ability to give with carbamide crystalline adducts in which there are about 8 $(NH_2)_2CO$ molecules per 10 carbon atoms. Because of their straight-chain structure, *n*-paraffins are also capable of penetrating the tiniest pores of molecular sieves (zeolites) and being adsorbed by them. All these properties are used to separate paraffins from their mixtures with hydrocarbons of other classes.

When derived from petroleum products, *n*-paraffins are produced as mixtures, of which the so-called soft and solid paraffin waxes are important. Soft paraffin wax melts at temperatures of up to $100^\circ C$. It is composed of the C_{11} - C_{20} hydrocarbons which boil in the temperature range from 200 up to $320-350^\circ C$. For certain purposes, soft paraffin wax is produced as a narrower fraction, say, in the range of $250-300^\circ C$. Solid paraffin wax (m.p. higher than $50^\circ C$) consists of hydrocarbons ranging from C_{20} to C_{35} , which boil between $300-350$ and $450-500^\circ C$.

1.1.1. Derivation of Lower Paraffins from Natural and Casinghead Gases

The main sources of the lower members of the paraffin series (C_1 - C_5) are natural and casinghead gases.

Natural gases are gases produced from gas fields. Sometimes they contain large quantities of carbon dioxide, nitrogen, helium, but the combustible hydrocarbon gases consist at least of 50 percent (by volume) of hydrocarbons. The *casinghead* gas is the gas that

accompanies the crude oil pumped from the oil well. Part of the associated gas is separated in special separators and the remainder is left dissolved in the crude oil and is distilled off upon stabilization, i.e., during the separation of volatile components (the stabilization gases). All these gases are composed mainly of the lower members of the paraffin series. Their typical composition, which varies with the oil field, is given in Table 1.2.

TABLE 1.2. The Composition of Natural and Casinghead Gases

Gas	Content, percent by volume					
	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂	N ₂ , etc.
Natural	80-97	0.5-4	0.2-1.5	0.1-1.0	0-1	2-13
Casinghead, after separators	40-75	5-20	2-20	1-7	0.5-5	5-18
Oil stabilization	5	10	20-30	30-40	15-25	—

Natural gas is used only as a source of methane, since it contains a small amount of the higher homologues. The casinghead gas and oil stabilization gases are the most valuable raw materials for the production of the C₃-C₅ paraffins. Of the C₄ hydrocarbons, the casinghead gas predominantly contains *n*-butane (3-5 volumes per 1 volume of isobutane) and of the C₅ members, only *n*-pentane (1.5-4 volume per 1 volume of isopentane).

Derivation of the Fraction of the C₃-C₅ Hydrocarbons from the Casinghead Gas. When the associated gases are processed, the heavier hydrocarbons (C₃-C₅) are isolated first. For this purpose, various methods can be used (condensation, adsorption, absorption) which are always combined with the fractional distillation to derive the individual hydrocarbons.

The *condensation-fractionation* method (or low-temperature fractionation) consists in the simultaneous use of high pressure and low temperature during the liquefaction and fractionation of gases. However, this method has not found wide application for the derivation of the C₃-C₅ hydrocarbons because of the high power consumption required to liquefy and cool the gases, since one of the columns must be refluxed with liquid ethane.

In the *adsorption-fractionation* method of separation of the casinghead gas, use is made of continuously operating adsorbers with a layer of activated charcoal moving downwards (the *hypersorption*). For the hydrocarbons to be desorbed, charcoal is treated with steam and then dried with the hot gas. The higher paraffins are first adsorbed by charcoal, which allows the C₅, C₄, C₃ and even C₂ fractions to be isolated. Because of the high capital investment and difficul-

ies associated with the transportation of the adsorbent and the operations involved, this method has not become widespread; however, it is considered to be the most efficient one for the separation of gases with a low content of C_3 - C_5 hydrocarbons.

The *absorption-fractionation* technique is widely employed for the processing of the casinghead gas. The principle of this technique consists in the following: the gas is washed in the absorber under pressure and on cooling with an absorbent—the “absorbing oil” (in this case the C_3 - C_5 hydrocarbons are mainly derived), following which the gases dissolved in the absorbent are distilled off and, after condensation, are subjected to further fractional distillation. The regenerated absorbent is cooled and returned to the absorber.

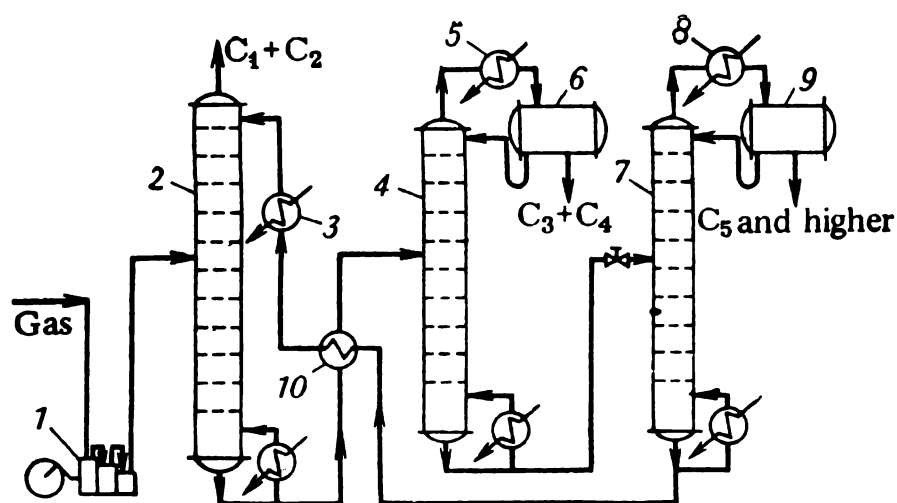


Fig. 1.1. Flowsheet of the absorption separation of the casinghead gas:
1—compressor; 2—absorption-stripping column; 3—cooler; 4, 7—desorbers; 5, 8—condensers; 6, 9—collectors; 10—heat exchanger.

Due to the use of the absorbent the partial pressure of the C_3 - C_5 hydrocarbons is considerably lowered and for these hydrocarbons to be separated from the lower homologues there is no need for the high pressure and low temperature required in the condensation-fractionation technique. This makes the absorption-fractionation technique more economical. When the process is operated with a high degree of propane extraction, a considerable amount of ethane is also unavoidably absorbed during the absorption process, and a large amount of higher hydrocarbons may be entrained by the ethane at the desorption stage. In order to avoid their repeated absorption-desorption, the absorption of the higher hydrocarbons is combined in a single apparatus with the stripping of light hydrocarbons from the saturated absorbent.

The technological scheme of the absorption separation of casinghead gas by using such absorption-stripping columns is shown in Fig. 1.1. The feed gas is compressed by a three-stage compressor 1 up to 1.2-2 MPa, depending on the content of higher hydrocarbons.

The gas is then delivered to the middle section of the absorption-stripping column 2 refluxed by the previously cooled absorbent (the heavier fractions of gasoline or ligroin are usually used as absorbent). The top of the column operates as an absorber, the C_5 and higher hydrocarbons being completely absorbed from the gas and about 95 percent of butanes and 70-80 percent of propane. The unabsorbed gases, which consist essentially of methane and ethane, can be used as fuel gas or methane, ethane and propane can be separated from them by one of the techniques described above. The absorption process proceeds with the liberation of heat, which is why the top of the column is cooled at several points with the aid of coolers not shown in the diagram.

In the bottom of the column 2 the methane and ethane dissolved in the absorbent at the absorption stage are distilled off from it. The C_3 and higher hydrocarbons entrained by them during stripping are again absorbed at the top of the column, which prevents their loss with the light gases. The saturated absorbent containing a small amount of ethane runs down into the column still.

The saturated absorbent passes from the still of column 2 into heat exchanger 10, where it is heated by the hot regenerated absorbent, and is led into desorber 4 designed for the distillation of the $C_3 + C_4$ hydrocarbons. It operates as an ordinary fractionating column, being heated at the bottom by spent steam and refluxed at the top by the liquid propane-butane fraction. The elevated pressure in the desorber (1.1-1.2 MPa) provides the condensation of the overhead product by water in condenser 5. The condensate runs down into collector 6 of the propane-butane fraction; part of the condensate is used to reflux column 4 and the remainder is drawn off from the apparatus as liquefied gas or is subjected to fractional distillation to separate the individual hydrocarbons.

The still liquid of desorber 4 is passed through the throttle valve, which reduces the pressure to nearly atmospheric, to a second desorber 7. Here the C_5 and higher hydrocarbons (the so-called *natural gasoline*) are distilled off and after being condensed in apparatus 8 flow into collector 9. Part of natural gasoline goes to reflux column 7, the remainder being drawn off from the system as finished product or is delivered for the further isolation of the pentanes. The still liquid from desorber 7 is the regenerated absorbent. It is cooled in heat exchanger 10 and cooler 3 and is then returned to the upper plate of absorption-stripping column 2.

Derivation of Individual Hydrocarbons. The propane-butane fraction isolated from casinghead gas is separated by fractionation at elevated pressure, which allows the use of water cooling to produce a reflux. First, the propane fraction is distilled off in the first column at 1.7-1.8 MPa and then isobutane and *n*-butane are separated in the second column at 0.7-0.9 MPa. The difference in boiling point

between these isomers is 11.6 °C and they are separated fairly well in a column with 50 plates.

The isolation of the pentanes from natural gasoline is effected by means of simple distillation. First, the mixture of isomeric pentanes is distilled off and then separated in the next column. The boiling points of these isomers differ only by 8 °C, therefore for a clear-cut fractionation to be effected, a column with 80-100 plates is required.

Ethane can then be isolated by fractional distillation from the residual gases left after the processes of absorption separation of casinghead gas. As regards methane, in the case of natural gas containing 96-97 percent of CH_4 , it is possible to use natural gas as technical methane. The gases containing methane, ethane, and a small amount of higher hydrocarbons are separated by the condensation-fractionation technique using high pressure and low temperature (low-temperature fractionation). To produce a reflux one has in such cases to resort to cooling with liquid propane and ethane at 4-4.5 MPa and higher pressures.

The paraffinic hydrocarbons intended for synthesis purposes must be sufficiently pure, since the impurities of the homologues require an extra consumption of the reactants and contaminate the end products. According to the existing requirements, the content of the basic substance in the fraction produced must range from 96 to 99 percent, depending on the field of its application.

1.1.2. Derivation of Higher Paraffins from Petroleum Products

The main source of liquid and solid paraffinic hydrocarbons used in the processes of organic synthesis is crude petroleum.

As known, crude oil consists mainly of paraffinic, naphthenic and aromatic hydrocarbons with a lesser or greater amount of oxygen-containing and sulphur compounds. The ratio of the hydrocarbons mentioned above varies considerably with the place of origin.

Each of the hydrocarbon classes is represented in crude oil by numerous homologues and isomers: paraffins are present as normal (straight-chain) and branched-chain isomers; naphthenic hydrocarbons are present as five- and six-membered homologues with one or more alkyl groups of varying length; aromatic hydrocarbons are contained as benzene and its homologues (toluene, xylenes, etc.); there are also other aromatic hydrocarbons with condensed rings (naphthalene, anthracene, and their homologues).

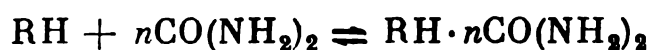
The initial stage in petroleum processing is direct distillation at atmospheric pressure (*atmospheric distillation*), in which the following fractions are separated from petroleum: petrol or gasoline (40-200 °C), ligroin (150-250 °C), kerosene (180-300 °C), gas oil (250-

360 °C). The residue left from atmospheric distillation (fuel oil) is then subjected to *vacuum distillation* to produce lubricating oils with varying volatility and viscosity (solar oil, spindle oil and transformer oil, etc.).

The lubricating oils and gas oil and kerosene fractions may contain up to 30 percent of *n*-paraffins. Several methods are employed to separate them.

The crystallization technique is used in two versions: with and without solvents. Crystallization without solvents is possible for gas oil and low-viscosity lubricating oils. The fraction is chilled with brine and crude or slack wax which contains about 30 percent of liquid hydrocarbons is separated. For these liquid hydrocarbons to be separated, "sweating" is carried out: the crude wax is placed on a sieve-plate and heated to produce a comparatively pure wax. The solvent crystallization technique is more widespread, the solvent used being a mixture of lower ketones and aromatic hydrocarbons. The fraction is dissolved and cooled down to -5 to -30 °C; the precipitate is subjected to recrystallization from the solvent. Crystallization with liquid propane as solvent is also practiced, the liquid propane being also used as a cooling agent; when it is partly evaporated, uniform cooling is achieved and the wax is crystallized.

Carbamide deparaffination consists of the separation of *n*-paraffins as crystalline adducts with carbamide. If the petroleum fraction is blended with a saturated aqueous solution of carbamide at 10-40 °C, a precipitate will separate out, which after being filtered off and treated with hot water or steam at 70-100 °C breaks down with the liberation of carbamide and a mixture of *n*-paraffins:



When paraffin-rich fractions are treated, use is made of a solvent (methylene chloride) to avoid thickening of the mixture. Carbamide deparaffination is applicable to any fractions and does not require low temperatures. Its shortcoming is low selectivity.

In the paraffin obtained by these two techniques, the content of up to 0.5 percent of aromatic hydrocarbons, 0.01 percent of sulphur and not more than 10 percent of isoparaffins is permissible.

Derivation of *n*-paraffins by means of zeolites is a new promising method, which finds an ever increasing application. It can be applied to any fractions and provides a high degree of extraction of *n*-paraffins (80-98 percent), which are obtained in a very pure state (98 to 99.2-percent purity). The process involves two stages: the adsorption of *n*-paraffins and desorption, which can be carried out in the gas or liquid phase at a temperature of up to 300-350 °C and various pressures. The desorption of the paraffins can be effected by lowering the pressure, increasing the temperature and by displacing with

ther substances (*n*-pentane, ammonia) or by using a combination of these techniques.

One of the schemes of this process (the Parex method) is given in Fig. 1.2. The feed petroleum fraction is mixed with a carrier gas (nitrogen) and heated in its stream and evaporated in heater 1. The resulting gas-vapour mixture is fed into one of the three adsorption units 2 filled with zeolite, where adsorption of *n*-paraffins

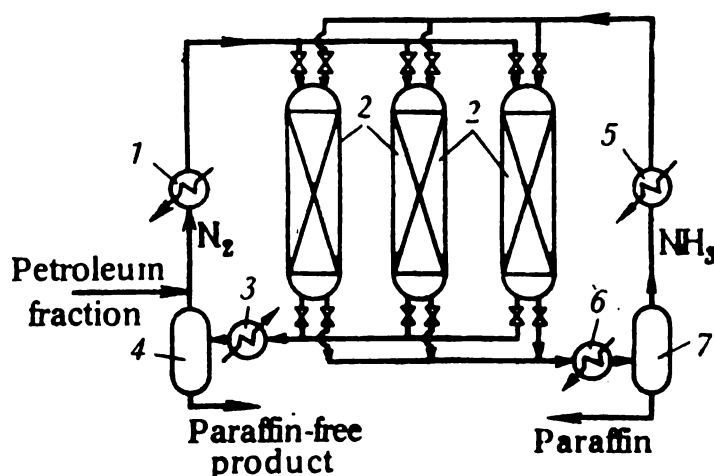


Fig. 1.2. The Parex method of isolation of *n*-paraffins:
1, 5—heaters; 2—adsorbers-desorbers; 3, 6—coolers; 4, 7—separators.

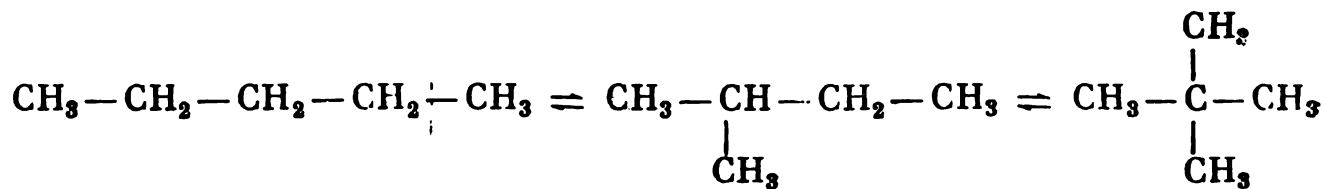
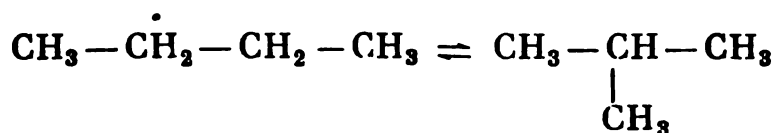
takes place. The mixture leaving the adsorber is cooled in cooler 3 and the paraffin-free condensate is separated from the carrier gas in separator 4, the carrier gas being returned to be mixed with the feed fraction. When the adsorbent is completely saturated with the paraffin, the mixture of the carrier gas with the feed fraction is passed to the second adsorber, in which the desorption stage has been carried out, and the gas desorbent (ammonia) preheated in heater 5 is passed to the first adsorber. After desorption the desorbent-paraffin mixture is cooled in cooler 6 and separated in separator 7, the ammonia being recycled to desorption. Of the three adsorption units, one operates at the adsorption stage and the other two at the desorption stage, the streams being switched over automatically.

1.3. Isomerization of Paraffins

The isomerization of paraffins is an extra source of isobutane and isopentane. Isomerization reactions play also an important role in certain processes of petroleum refining (catalytic cracking and catalytic reforming), when *n*-paraffins are isomerized to branched-chain hydrocarbons, which have a higher octane number.

These reactions are reversible processes, in which a thermodynamic equilibrium is set up between normal paraffins and isopa-

raffins:



How the content of isoparaffins in the equilibrium mixture upon isomerization of *n*-butane and *n*-pentane varies with temperature can be seen from the data presented in Fig. 1.3. As can be seen from

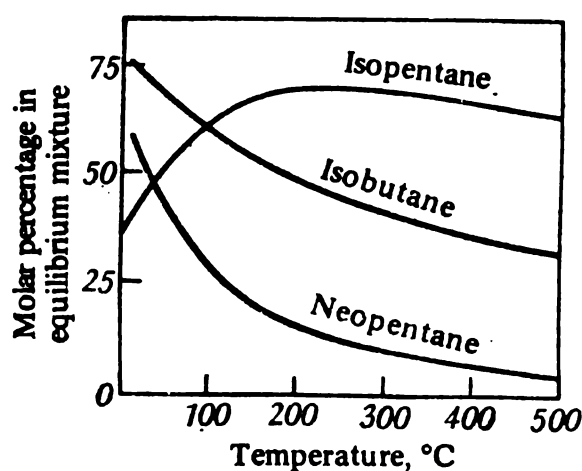


Fig. 1.3. Temperature dependence of the equilibrium content of isobutane, isopentane, and neopentane in a mixture upon isomerization of the corresponding hydrocarbons.

this figure, in the equilibrium mixture obtained by the isomerization of *n*-butane the content of isobutane decreases continuously with increasing temperature. In the isomerization of pentanes, the same decrease in content is observed for neopentane, whereas the content of isopentane passes through a maximum at 180-200 °C. This is evidence that at low temperatures the most stable of the hydrocarbons with an open chain is the most branched-chain isomer and at high temperatures, *n*-paraffin.

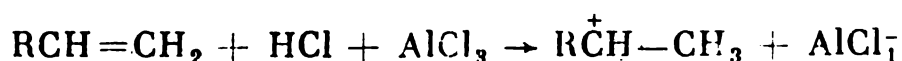
The isomerization of paraffins can be carried out using aluminium

chloride or bifunctional catalysts consisting of metals of the platinum group with an acid-type support (aluminium oxide, aluminosilicate, zeolite).

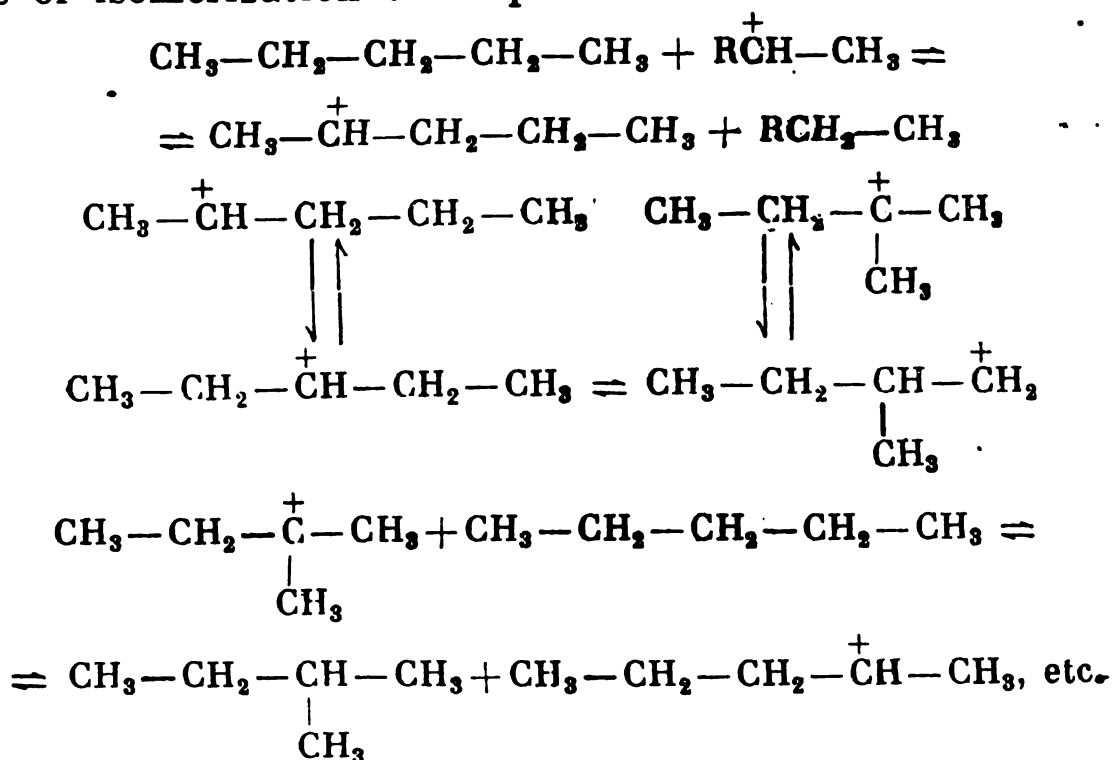
The isomerization reaction proceeds by an ionic mechanism via the intermediate formation of carbonium ions. First, as a result of the cracking of the paraffin or of its dehydrogenation, there are obtained olefins. From these, on a heterogeneous catalyst with its active centres playing the role of proton donors, there are formed carbonium ions:



For the isomerization reaction to be conducted efficiently in the presence of aluminium chloride, a co-catalyst is required—hydrogen chloride, since carbonium ions are formed only when the olefin is jointly acted on by aluminium chloride and hydrogen chloride:



The carbonium ions are capable of detaching hydrogen atoms (as hydride ions) from the other hydrocarbon molecules and of being isomerized with the displacement of the hydrogen atoms or alkyl groups inside the molecule. As a result, the following ionic-chain process of isomerization takes place:



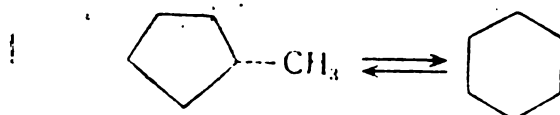
The isomerization of paraffins is always accompanied by side breakdown reactions (cracking), polymerization and alkylation, as a result of which the isomerization products contain lower-boiling hydrocarbons and a small amount of higher hydrocarbons. It is evident that these side processes are undesirable where the isomerization reaction is to be directed exclusively to the isoparaffins. In order to suppress these processes, the appropriate temperatures and contact time have to be chosen.

The isomerization was originally conducted only with aluminium chloride as catalyst, which was used in the solid state, in the form of a liquid complex with hydrocarbons (plus HCl) or as a solution in antimony trichloride, which does not dissolve in an excess of paraffin. The hydrocarbon feedstock is preliminarily saturated with hydrogen chloride and passed to a reactor with a mixer or to a column with a catalyst countercurrent, where the isomerization takes place under pressure and at 80-120 °C. The hydrocarbon layer is separated from the catalyst, the HCl is distilled off and neutralized, following which fractional distillation is accomplished, the unconverted feedstock being returned to isomerization.

Bifunctional catalysts (say, 0.5-1 percent of Pt or Pd on Al_2O_3) are less active and operate at 350-450 °C when the equilibrium is not so favourable for the formation of isoparaffins. In this version the process resembles the reforming of petroleum products (see Sec. 1.3.1.2). It is operated in an adiabatic flow reactor at 2-4 MPa

in excess hydrogen (the molar ratio of hydrogen to hydrocarbon is from 2 : 1 to 3 : 1). This prevents the dehydrogenation of the paraffins and the polymerization of the olefins with the result that the catalyst is not contaminated with tarry substances. After being condensed and separated from the circulating hydrogen the reaction products are subjected to fractionation; the unreacted *n*-pentane is recycled and the isopentane is isolated as a commercial product. The degree of conversion of *n*-pentane per pass through the reactor is 50-60 percent and the total yield of isopentane exceeds 90 percent.

The naphthenic hydrocarbons are isomerized in the same way as the paraffins, when there is observed, for example, the reversible conversion of methylcyclopentane to cyclohexane:



In the United States this process is used for the processing of the gasoline fraction rich in the C_6 naphthenes, which gives an additional source for the production of cyclohexane.

1.2. Olefins

Olefins, or alkenes, which are used as the feedstock for basic organic and petrochemical synthesis, may be divided into two principal groups: (1) the lower gaseous or low-boiling olefins from ethylene to amylenes (C_2 - C_5) and (2) the higher olefins from C_6 to C_{12} - C_{18} (mainly C_7 - C_{15}), which are usually not individual compounds but mixtures of the isomers and homologues.

Lower Olefins. The olefinic hydrocarbons from ethylene to butylenes are gases under ordinary conditions, and the amylenes, C_5H_{10} , are low-boiling colourless liquids. Some properties of these hydrocarbons are given in Table 1.3. From the data on the critical temperature it is clear that ethylene can be converted to the liquid state only at low temperatures and high pressures by cooling, say, with boiling ammonia. The other gaseous olefins are liquefied under pressure, this time by cooling with water. When comparing olefins (or alkenes) with the corresponding paraffinic hydrocarbons it can be seen that ethylene boils below ethane by $15^\circ C$ and propylene below propane by $5.5^\circ C$ (see Table 1.1). This is very important for refining processes, where ethylene (and propylene with great difficulty) is separated from the corresponding paraffins by fractional distillation. The boiling points of butylenes are very close to those of butanes, and simple fractionation is inefficient for their separation.

TABLE 1.3. Properties of the Lower Olefins

Olefin	Formula	Condensation temperature, °C	Critical temperature, °C	Critical pressure, MPa	Maximum permissible concentration in mixture with air, % by vol.
Ethylene	$\text{CH}_2=\text{CH}_2$	-103.7	9.9	4.95	3.0-32
Propylene	$\text{CH}_3-\text{CH}=\text{CH}_2$	-47.7	91.8	4.47	2.2-10.0
1-Butene	$\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$	-6.3	146.2	3.89	1.6-9.4
<i>cis</i> -2-Butene	$\text{CH}_3-\text{C}=\text{C}-\text{CH}_3$ H H	+3.7	157.0	4.02	1.6-9.4
<i>trans</i> -2-Butene	$\text{CH}_3-\text{C}=\text{C}-\text{CH}_3$ H H	+0.9	—	—	1.6-9.4
Isobutylene	$\text{CH}_3-\text{C}=\text{CH}_2$ CH_3	-7.0	144.7	3.85	1.8-9.6
<i>n</i> -Pentenes	<i>n</i> -C ₅ H ₁₀	30-37	—	—	1.3-8.8
Isopentenes	<i>iso</i> -C ₅ H ₁₀	20.1-38.6	—	—	1.3-8.8

All the lower olefins form an explosive mixture with air (oxygen); the plant departments where these hydrocarbons are produced or used as raw material are classified as belonging to the A category in respect to fire hazard. In toxicity the olefins are close to the saturated hydrocarbons (they cause narcotic effects when the vapours are inhaled); their maximum permissible concentration in the atmosphere of industrial premises is the same as for the corresponding paraffins.

The important features that distinguish the olefins from the paraffins with the same number of carbon atoms are their higher solubility and their sorption ability, the latter being due to the presence of an unsaturated carbon-carbon bond. The olefins are adsorbed better than the paraffins by solids, are absorbed by cuprammonium solutions and dissolve in polar liquids, such as acetone and furfural. Therefore, the lower olefins have to be isolated by means of special methods, among which extractive distillation has become of utmost importance. Its principle is as follows: in the presence of a third component, which has a lower volatility and is capable of undergoing a dipole-dipole interaction or forming various complexes with the olefins, the partial pressure of the olefins is lowered to a greater extent than in the case of the paraffins. As a result, the

relative volatility of the paraffins measured by the ratio of the saturated vapour pressures, $\alpha = P_A/P_B$, increases considerably (Table 1.4).

TABLE 1.4. Relative Volatilities of the C_4 Hydrocarbons as Compared with 1,3-Butadiene

Hydrocarbon	Relative volatility			
	in simple distillation	in extractive distillation		In chemisorption with solutions of cupric salts*
		with furfural	with acetonitrile	
Isobutane	1.209	2.600	—	—
Isobutylene	1.070	1.666	1.58	35
1-Butene	1.046	1.718	1.56	10
1,3-Butadiene	1.000	1.000	1.00	1.00
<i>n</i> -Butane	0.871	2.020	—	—
<i>trans</i> -2-Butene	0.843	1.190	1.34	54
<i>cis</i> -2-Butene	0.776	1.065	1.28	25

* In chemisorption with aqueous solutions of cuprammonium complexes used to purify the C_4 fractions from 1,3-butadiene or to separate the latter from the C_4 fractions.

The Higher Olefins. The $C_6 - C_{18}$ olefins are liquids, whose boiling temperature depends on the number of carbon atoms and the chain structure. Below are given the boiling points (in $^{\circ}C$) of the $C_6 - C_{12}$ olefins with a straight chain:

$n-C_6H_{12}$	63.5-68	$n-C_{10}H_{20}$	170-175
$n-C_7H_{14}$	93.8-98.2	$n-C_{12}H_{24}$	213-218
$n-C_8H_{16}$	121-126			

Olefins with a branched chain of carbon atoms boil at a lower temperature than their straight-chain isomers.

Because of the high reactivity and relative accessibility, the olefins have become dominant as starting materials for organic synthesis. The most important of them are ethylene and propylene, whose production in the USA is, respectively, 11 and 6 million tons per year. The butylenes and higher olefins are used on a smaller scale, and the isoamylenes on the smallest scale.

The principal industrial method of olefin production is the cracking of petroleum fractions or hydrocarbon gases. This process may be divided into two groups: thermal (pyrolysis and thermal cracking of paraffin) and catalytic (catalytic cracking). The former are effected for the production of olefins, and the latter for the manufacture of gasoline with olefins as by-products. Moreover, part of the olefins is

prepared by the dehydrogenation of the corresponding paraffins, and some olefins by reactions of their interconversion (oligomerization and disproportionation).

1.2.1. Theoretical Foundations of Cracking and Pyrolysis

Thermodynamic Stability of Hydrocarbons. An important role in the estimation of the feasible conversions of hydrocarbons during processing is played by their thermodynamic stability.

Figure 1.4 shows the temperature dependence of the Gibbs free energy (or the Gibbs function) of formation of C_6 hydrocarbons of

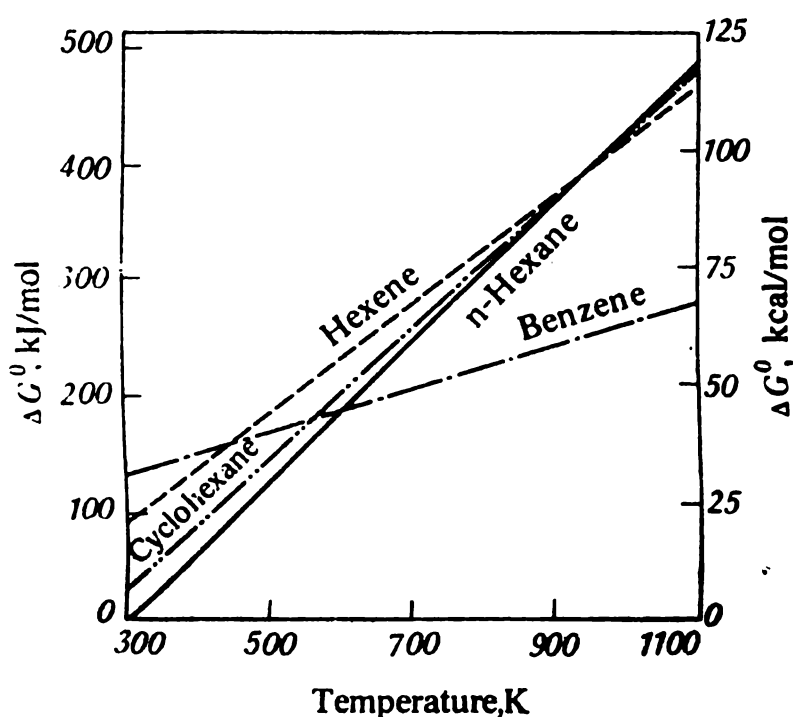


Fig. 1.4. Temperature dependence of the Gibbs free-energy change ΔG° in the formation of C_6 hydrocarbons from simple substances.

various classes from simple compounds. The Gibbs free energy of their interconversion (ΔG°) related to the equilibrium constant K_P by the equation

$$\Delta G^\circ = -RT \ln K_P$$

and equal to the difference of the ordinates of the corresponding curves in Fig. 1.4 is a measure of the thermodynamic feasibility of the process, since the system always tends to a state with the lowest Gibbs free energy. As can be seen in the case of the C_6 hydrocarbons, at low temperature the thermodynamic stability of hydrocarbons of various classes with the same number of carbon atoms in the molecule decreases in the following sequence:

$$\text{Paraffins} > \text{Naphthenes} > \text{Olefins} > \text{Aromatics}$$

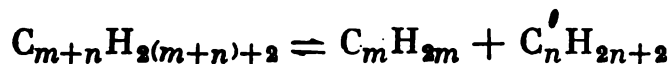
However, with increasing temperature, because of the different temperature dependences of the standard Gibbs free energy, the

order is reversed:



Thus, with the thermal action on petroleum products the group composition of the hydrocarbons should be expected to change.

The breakdown (cracking) of a paraffin may take place with the formation of olefin or paraffin molecules with a shorter chain of carbon atoms, the reverse process being the alkylation of a paraffin by an olefin:



The thermodynamic feasibility of these reactions is illustrated by a plot of the Gibbs free energies of these reactions against temperature (Fig. 1.5). It is easy to see

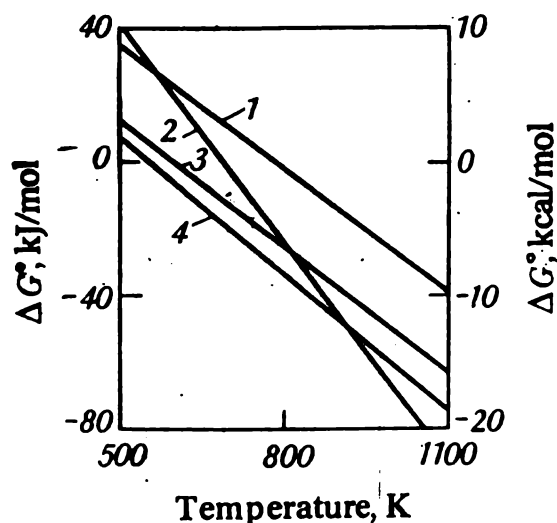
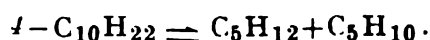
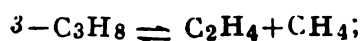
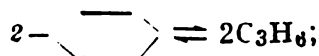
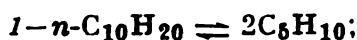


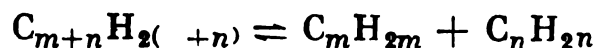
Fig. 1.5. Temperature dependence of the free-energy change for the decomposition of various hydrocarbons:



that at temperatures of up to about 600 K the change in ΔG° is greater than zero and, hence, the cracking of paraffins is thermodynamically infeasible, the only possible reaction being alkylation. At a higher temperature the situation is reversed, and at 800 K upwards the cracking process becomes practically irreversible. It is essential that *n*-decane and, in general, the higher paraffins are more liable to undergo cracking than the lower paraffins (curve 4 lies below curve 3).

For olefins (curve 1 in Fig. 1.5) the tendency to undergo cracking manifests itself at a higher temperature than in the case of paraffins. In the system of reversible

cracking of an olefin and its dimerization (polymerization)



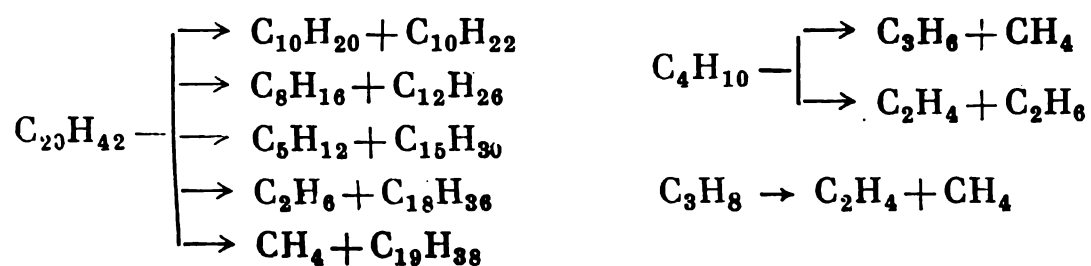
the change of the sign in the change of ΔG° for the lower olefins occurs only at 750-800 K. This is an indication of the thermodynamic feasibility of their polymerization on thermal and catalytic cracking, but with the preponderance of cracking at higher temperatures.

Figure 1.5 (curve 2) shows also the dependence of the change of the Gibbs free energy, ΔG° , for the breakdown of the cyclohexane molecule into two propylene molecules. An analysis of this curve shows

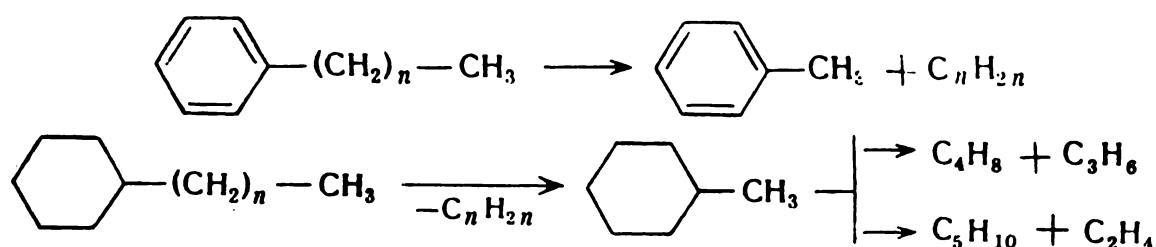
that at elevated temperatures (higher than 650-700 K) the cracking of naphthenes with the formation of open-chain hydrocarbons becomes possible.

The laws of thermodynamics allow one to assess the role of pressure in the thermal cracking of petroleum products. An increase in pressure favours the shift of equilibrium towards the polymerization of olefins and the alkylation of paraffins, since these reactions proceed with a reduction in volume. Because of this, a high pressure prevents a deep cracking of the raw material and lowers the formation of lower hydrocarbons and, especially, of olefins. Obviously, a decrease in pressure and an increase in temperature must act in the reverse direction.

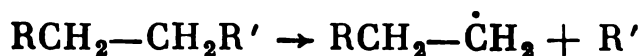
Chemical Reactions Involved in Thermal Cracking and Pyrolysis. The most important reaction in thermal processes is the cracking of hydrocarbons at carbon-carbon bonds. This reaction and also the subsequent cracking of the primary products yield gaseous and liquid mixtures of saturated and unsaturated hydrocarbons:



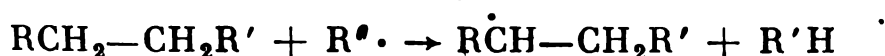
The cyclic hydrocarbons present in petroleum products split off side chains under similar conditions and the naphthenic rings, in addition, open with the formation of olefins:



In the absence of catalysts all the reactions indicated above proceed via the formation of free radicals and are chain processes. The chain is generated upon absorption of a quantum of energy or upon collision of the molecule with the wall:

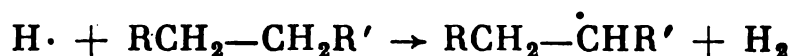
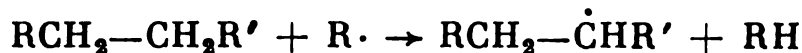


and is then continued as follows:

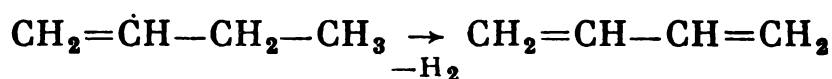


As the temperature increases the cracking proceeds more deeply but is accompanied by dehydrogenation and cyclization reactions.

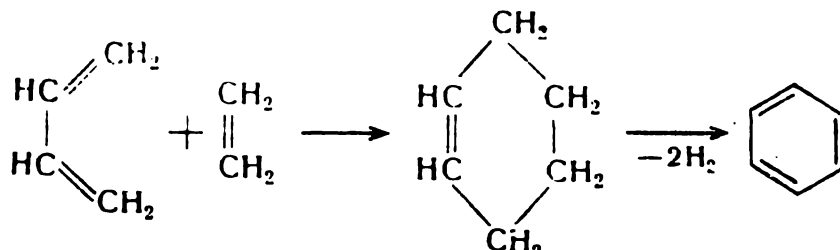
Dehydrogenation also proceeds as a radical-chain process:



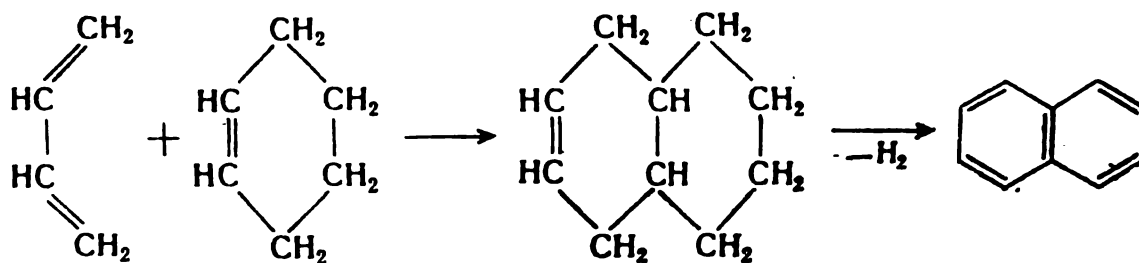
Dehydrogenation at 600-650 °C leads to the formation of very reactive dienic hydrocarbons, say 1,3-butadiene:



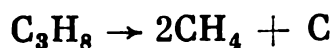
Upon interaction of the dienes with olefins (the diene synthesis) straight-chain hydrocarbons undergo cyclization and the resulting cyclo-olefins are aromatized:



From the dienes and cyclo-olefins there are thus obtained condensed aromatic hydrocarbons, say naphthalene:

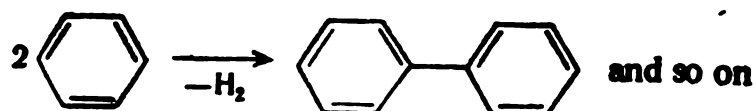


Apart from the gaseous and liquid compounds, all high-temperature processes of refining of petroleum products and hydrocarbon gases give also solid compounds—carbon black or coke. The formation of carbon black is accounted for by the decomposition of hydrocarbons to free carbon, as, for example, in the following reactions:



Coke results from the deep condensation of aromatic compounds which proceeds with the elimination of hydrogen (dehydroconden-

ation):



This leads to the formation of highly condensed nonvolatile and insoluble substances, of which coke is composed.

The Yield and Composition of Products of the Thermal Breakdown of Hydrocarbons. The relative yield of liquid products (gasoline and cracked residue or pyrolysis tar), gas (cracked gas or pyrolysis gas) and solid residue (coke or carbon black) depends on three principal factors: the raw material, temperature, and contact time.

Various types of raw material differ by the hydrogen to carbon ratio: there are 3 hydrogen atoms per carbon atom in ethane, 2.5 in

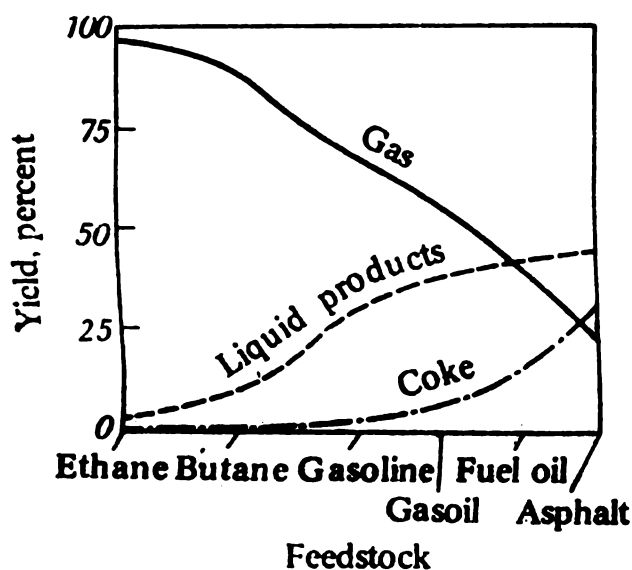


Fig. 1.6. The yield of products in the pyrolysis of various raw materials at 800 °C.

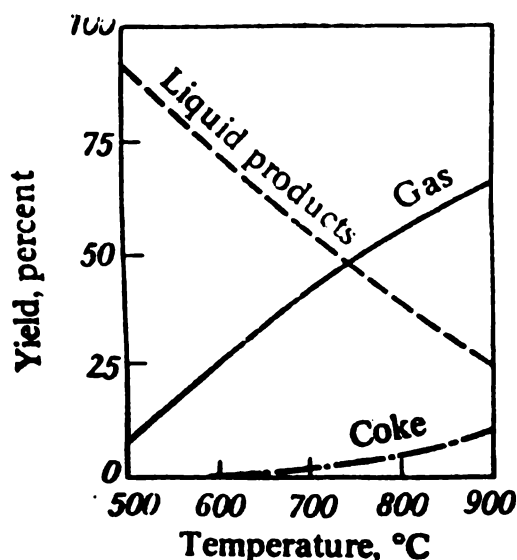


Fig. 1.7. Temperature dependence of the yield of products in thermal decomposition of gasoil.

butane, 2 in cyclohexane, and even less in aromatic components. Evidently, a relatively light raw material (hydrocarbon gases and gasoline) will give more gas and little coke on cracking; by contrast, heavy hydrocarbons with a high carbon content (especially those containing many aromatic components) will yield a considerable quantity of coke and a smaller amount of gas (Fig. 1.6).

Another important factor which has an impact on the product yield is temperature. Thermal cracking of higher hydrocarbons starts at about 400 °C but attains a considerable rate only at 480-550 °C, being speeded up with further increase in temperature. The general regularity here is that, other conditions being equal, the yield of gas and coke increases and the yield of liquid products decreases as the temperature rises (Fig. 1.7).

The composition and yield of the products also mainly depend on temperature. As the temperature increases the liquid cracked

products are increasingly enriched with aromatic compounds and the gas with hydrogen and lower hydrocarbons. For example, thermal cracking of petroleum fractions at 500-550 °C gives a mixture of liquid compounds, which differ from the feed fraction mainly by the appearance of olefins in them, and the gas produced consists mainly of C_3 — C_4 hydrocarbons with a total yield of olefins of about 4 percent of the feedstock. An increase in temperature up to 750-850 °C results in the liquid products being aromatized by 85-95 percent and the amount of C_2 — C_4 paraffins in the gas is reduced and it becomes enriched in propylene and especially in ethylene. The total yield of C_2 — C_4 olefins reaches 60-80 percent by weight of the feedstock in the pyrolysis of ethane and propane and 40-50 percent (by weight) in the pyrolysis of gasoline. In the gaseous products there appear dienes and acetylenes, the yield of the most valuable butadiene from gasoline being 4-5 percent. As the temperature is increased further the yield of olefins, having passed through a maximum at 800-900 °C, begins to fall and the quantity of hydrogen and acetylene increases.

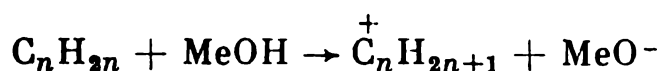
The composition of thermally cracked products is also strongly influenced by the contact time. Since the formation of hydrogen, methane, aromatic compounds and coke and also the polymerization of olefins are consequent to the primary cracking of the raw material, it follows that, other conditions being equal, an increase in contact time results in an intensified development of these processes and in a reduction in the yield of olefins. Pressure has nearly the same effect: as the pressure falls off the polymerization and condensation of the primary products are slowed down and the olefin yield increases.

Depending on the purpose of the process, an appropriate choice is made of the feedstock, temperature, contact time and pressure. For example, petroleum coke is made from the heavy residues under pressure at 500-550 °C and with a long reaction time. Where the reaction is to be directed exclusively to liquid products (gasoline or alpha-olefins), use is made of the middle fractions of crude petroleum, by carrying out the process at 500-550 °C and with the contact time that provides only a partial conversion of the feedstock with its unconverted portion being recycled. Finally, the pyrolysis designed specifically to produce lower olefins is accomplished at 800-900 °C, the contact time being short (0.2-0.5 s) and the raw material being diluted with steam. The choice of the feedstock for pyrolysis is very wide (from ethane to crude oil), but there is a growing trend to use, instead of the hydrocarbon gases, straight-run gasoline fractions, which provide an increased yield of butadiene and aromatic hydrocarbons, the valuable by-products of pyrolysis. Another tendency is to reduce further the contact time (0.1 s and less) and to develop the so-called "millisecond pyrolysis". In the pyrolysis of heavier petroleum fractions, hydropyrolysis carried out in the

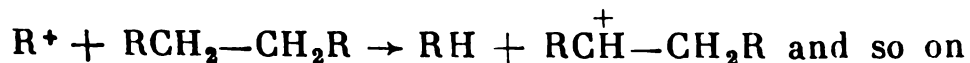
presence of hydrogen is a promising technique; hydrogen prevents the formation of coke and heavy residues, leading to an increase in the yield of olefins and butadiene.

Catalytic Cracking. In catalytic cracking, the breakdown of hydrocarbons is effected over aluminosilicates, which are typical catalysts of ionic reactions.

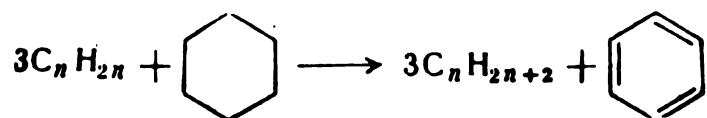
In the presence of these catalysts the cracking reactions proceed not by a free-radical mechanism, as is the case with thermal cracking, but by an ionic mechanism, via the intermediate step of positively charged carbonium ions. These ions are formed from olefins that are produced, though in a small amount, in the thermal cracking of the raw material, and from the protons generated by an acid-type catalyst:



Carbonium ions are unstable and capable of breaking down into an olefin molecule and a carbonium ion with a shorter carbon chain. Moreover, they can abstract hydrogen as a hydride ion from other neutral molecules, converting them also into carbonium ions. This starts an ionic-chain process of paraffin cracking:



In contrast to free radicals, carbonium ions are readily isomerized, as has already been mentioned. As a result, the catalytically cracked gasoline contains many isoparaffins having a higher octane number than the *n*-paraffins. This effect is even more enhanced because of the increased content of aromatic hydrocarbons, which are formed due to the catalytic redistribution of hydrogen between the molecules of the olefin and naphthene:



The composition of gases resulting from catalytic and thermal cracking is also different. In catalytic cracking, the breakdown of hydrocarbons to compounds with one and two carbon atoms proceeds only to a small extent, since the carbonium ions CH_3^+ and $C_2H_5^+$ are only slightly stable. Therefore, in gases produced by catalytic cracking there predominate the C_3 and C_4 hydrocarbons, but at the same time they contain more hydrogen than the gases from thermal cracking (the typical composition of catalytically cracked gases is given in Sec. 1.2.3). The yield of the gas in catalytic cracking is 0-15 percent (by weight).

1.2.2. Technology of Cracking and Pyrolysis

Pyrolysis of Liquid Petroleum Products and Hydrocarbon Gases. Pyrolysis is an endothermic process and belongs to the category of highly energy-consuming industries, where the utilization of the heat of hot gases is important. The existing designs of reaction units differ in the heating system: external heating with flue gases or with superheated steam (adiabatic pyrolysis); by partial burning of the feedstock in the presence of oxygen (oxidative pyrolysis); and heating with a solid, fixed or moving heat carrier (regenerative pyrolysis).

In the most widespread scheme of pyrolysis with external heating, the principal reaction unit is a tubular furnace used also for a number of other processes of petroleum processing and petrochemical

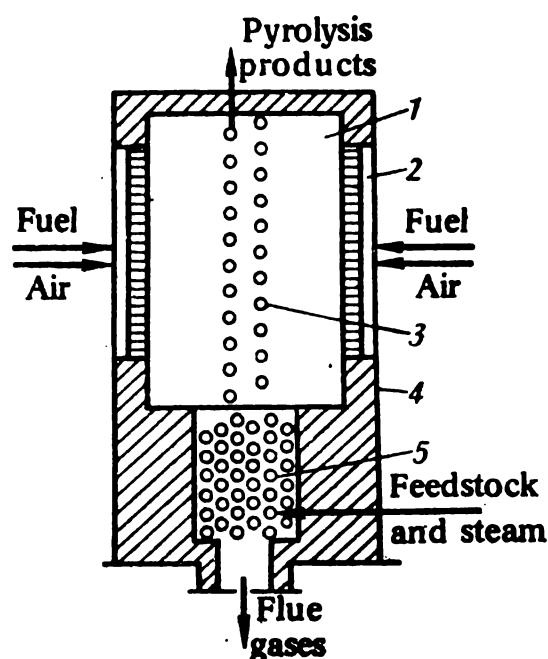


Fig. 1.8. Tubular furnace:

1—combustion chamber; 2—flameless burner; 3—radiant section tubes; 4—body; 5—convection chamber.

synthesis. The heating of the feedstock and pyrolysis are carried out in the furnace by the gases obtained on combustion of a gaseous or liquid fuel. Instead of the older low-capacity furnaces, an ever increasing use is being made of more powerful plants, which are distinguished by high thermal stress and reduced residence time of the feedstock (Fig. 1.8).

In these plants the fuel is burned in flameless burners 2, which consist of a series of channels in the ceramic lining of the furnace. When such burners are used, the flame does not get into combustion chambers 1, and the heat is radiated by the red-hot panel and

is transferred by combustion gases, which makes the furnace more compact and increases its efficiency. In the radiant section 3 heat transfer is accomplished due to radiation, the tubes being heated from both sides, which increases the thermal stress (in contrast to the older furnaces, where the tubes were arranged at the ceiling). The partially cooled flue gases are then passed into convection chamber 5, where heat transfer is effected by means of less effective convection. The vapours of the feedstock and steam are passed to the tube section in the convection chamber; they are heated to the required temperature and then transferred to the radiant section, where the pyrolysis takes place.

A further improvement was the development of gradient furnaces, in which heat transfer and heating intensity are controlled according

to the pyrolysis stage that takes place in a particular tube section. This modification has increased the capacity of tubular furnaces: from 3,000-4,000 up to 20,000 tons of ethylene per annum and enabled the development of a plant with a capacity of up to 300,000-450,000 tons of ethylene per year.

The pyrolysis furnaces can operate under various regimes: the ethylene, propylene, or butylene regimes, which differ in relative yield of the corresponding fractions which depends mainly on temperature. Because of the highest demand on ethylene, the operating conditions of the furnaces were gradually made more severe: from 700-750° up to 850-870 °C at the present time. In order to lower the partial pressure of the feedstock in the furnace, the water condensate in an amount of 0.3-0.6 kg per kg of hydrocarbons is fed into the furnace. The steam simultaneously converts part of the coke produced, but the coke is nevertheless gradually accumulated in the pipes, which is why the operation of the furnace is stopped after several months and the pipes are decoked.

The pyrolysis products have a temperature of 800-850 °C at the furnace outlet; on slow cooling of the gas this may cause the polymerization of olefins. Therefore, the so-called "quenching" is first carried out by spraying into the gases the water condensate, as a result of the evaporation of which the temperature rapidly falls down to 600-700 °C. This heat as well as the heat of the flue gases is then used to heat the charging stock and to produce steam required for pyrolysis. With modern high-capacity plants the utilization of the heat of pyrolysis products is more perfect: a boiler is used which gives high-pressure steam (10-12 MPa). This steam is used to drive the turbocompressors; hot water is also obtained, which is sent to heat the gas-separation columns, thus providing a closed water circulation system, which excludes the formation of toxic waste waters.

One of the modern technological schemes of the pyrolysis of gasoline and of the primary separation of the products is shown in Fig. 1.9. The pyrolysis is effected in a tubular furnace 1, the fuel and air being fed into the burners. The heat of the flue gases leaving the convection is utilized in heat exchangers 2, 3, and 4, where respectively the steam intended for pyrolysis is superheated, the gasoline is preheated and evaporated, and the water condensate used to produce steam is heated. After this, the flue gases are discharged through the stack to the atmosphere. The pyrolysis products leave the furnace and are led into the "quenching" apparatus 5; the water condensate is sprayed into it and the mixture is immediately cooled down to 650-700 °C due to the evaporation of the water condensate. The heat of the hot pyrolysis products is first used in waste-heat boiler 6 with a steam-collector 7 to produce high-pressure steam, the gases being cooled down to 350-400 °C. They are then cooled further

in column 8 and subjected to partial condensation by refluxing with the circulating "middle" oil. The coke and the heaviest pyrolysis products (tar) are collected in the still of column 8, and the hot "middle" oil is drawn off from one of the lower plates as liquid together with the fresh condensate of the middle fractions of the pyrolysis products. This oil is passed into steam generator 9, where its heat is used to produce steam to be led to heat-exchanger 2, and then passed for pyrolysis. The cooled middle oil is returned by circulation pump 10 to reflux column 8, but part of it is removed from the system and directed for further refining or is used as fuel.

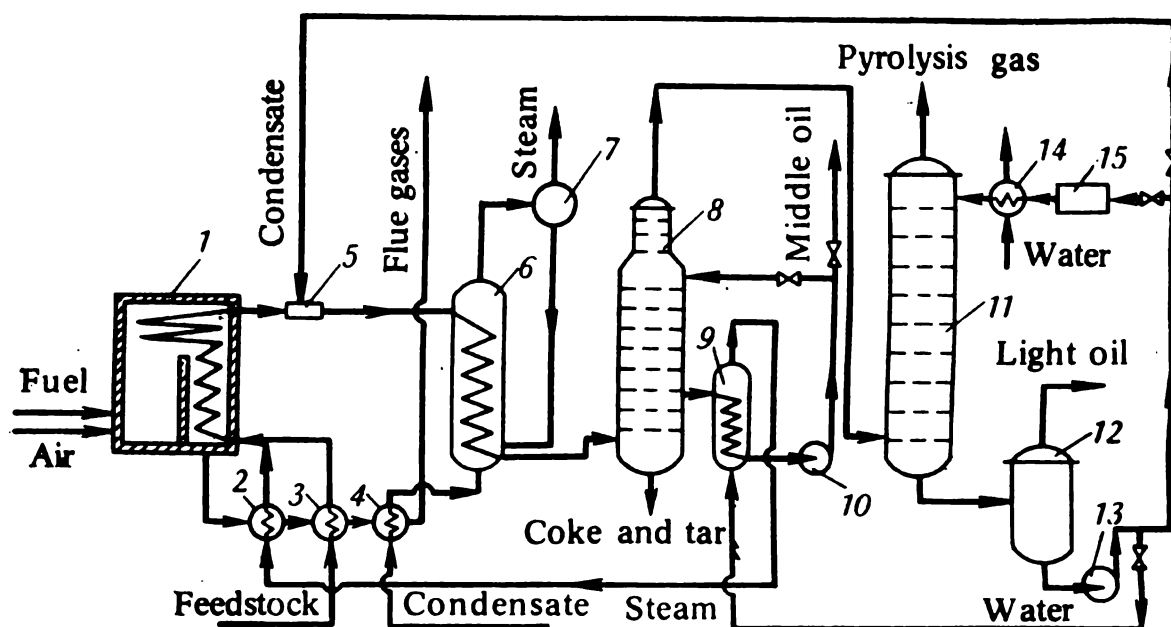


Fig. 1.9. Flow diagram of gasoline pyrolysis:

1—tubular furnace; 2, 3, 4—heat exchangers; 5—"quenching" unit; 6—waste-heat boiler; 7—steam collector; 8—column for distillation topping of "middle" oil; 9—steam generator; 10, 13—circulation pumps; 11—water scrubber; 12—separator; 14—cooler; 15—heat utilization system.

The pyrolysis gas in conjunction with the vapours of the lighter products and steam is taken from the top of column 8 at a temperature of 110 °C. This heat is used in scrubber 11 for heating the circulating water condensate, as a result of which the condensation of steam and "light" pyrolysis tar takes place, and the gas is cooled down to 30-35 °C and is then subjected to compression and further separation (it still contains a considerable amount of volatile vapours, but these are more efficiently entrapped under pressure). The mixture of hot water and "light" oil is led from scrubber 11 to separator 12, where the hydrocarbons are separated as the overhead and transferred for further refining—for the separation of aromatic compounds (benzene, toluene, xylenes). Part of the hot water condensate is delivered by means of circulation pump 13 to "quench" the pyrolysis products, and the remainder is circulated through the heat utilization system 15, cooled additionally in cooler 14 and returned for

cooling the pyrolysis products to scrubber 11. Part of the circulating water is passed for purification from tarry impurities, after which it is returned to the water circulation system or is used to produce steam required for pyrolysis.

Thermal Cracking of Paraffins. The thermal cracking of solid or soft paraffin wax is employed for the manufacture of liquid olefins with a straight chain of 5-20 carbon atoms. The technological scheme of the process is in many respects analogous to the pyrolysis and thermal cracking of petroleum products. The cracking process is also effected in a tubular furnace but at about 550 °C when no deep processes of condensation and aromatization take place. In order to increase the yield of olefins it is recommended to use steam. To avoid secondary reactions, the cracking is carried out to a small degree of conversion of the wax (20-25 percent), which is returned to the process after the separation of the light fractions.

The cracked products consist of a gas (about 20 percent) and liquid substances (the C_5 and higher hydrocarbons); there is also formed 1-2 percent of coke. Of primary importance are the liquid products, which are separated from the gas and distilled to isolate the various fractions. Below is given the typical fractional composition of the liquid products obtained by wax cracking (in percent of the converted feedstock):

up to 140°C (C_5-C_8)	. . 20
140-180°C (C_9-C_{10})	. . . 10-15
180-240°C ($C_{11}-C_{13}$)	. . 11-13
240-320°C ($C_{14}-C_{18}$)	. . 14-16

The content of olefins in these fractions is 70-80 percent. Of these 90-95 percent are olefins with a double bond at the end of the chain—alpha-olefins which are of special interest for the synthesis of surface-active substances (surfactants).

Catalytic Cracking. The main feature of catalytic cracking which determines its technological equipment is the rapid coking of an aluminosilicate catalyst, leading to the loss of its activity. As a result, in batch operations the catalyst has to be regenerated every 10 min by passing hot air through it in order to burn out the coke, the temperature of the air being strictly controlled in order to prevent the surface from being polished. The catalyst is heated up to 550-600 °C and may serve as a heat carrier in endothermic reactions of hydrocarbon cracking.

The improvement of the catalytic cracking process has taken the path of creating continuous systems. Cracking and regeneration are effected in two separate units, through which the catalyst is circulated. Wider application is now made of a variant of catalytic cracking in a fluidized bed of the catalyst (the *fluid-bed process*),

which makes use of a microspherical catalyst capable of being in the suspended state in the flow of the gases and vapours.

The design of the catalytic cracking unit using a fluidized bed of microspherical catalyst is given in Fig. 1.10. The regenerator 3

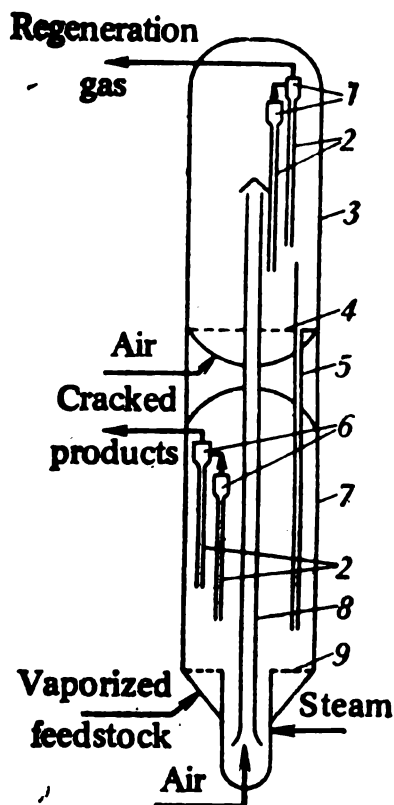


Fig. 1.10. The reaction unit in the fluid process:

1, 6—cyclones; 2—catalyst tubes; 3—regenerator; 4, 9—distributor grids; 5—overflow pipe; 7—reactor; 8—lift.

and reactor 7 are arranged one above the other in a single unit, which is a column up to 60-70 m high. The coked catalyst is lifted by hot air in central lift-pipe 8 to regenerator 3. The heated air to be used for burning off the coke is also led to regenerator 3 via distributor grid 4. In order to avoid overheating the regenerator is cooled with water at several places and the vapour obtained is used for other technological purposes within the same plant. The flue gases are separated in cyclones 1 from the entrained catalyst particles, which are carried down through pipes 2 back to the fluidized bed. The regenerated catalyst runs down pipe 5 into reactor 7, where the vapours of the hydrocarbon feedstock are led through distributor grid 9. The cracked products pass

through cyclones 6, where they are separated from the entrained catalyst particles and are directed for further processing. The spent catalyst is transferred to the stripping section, where the entrained hydrocarbons are removed by steam, and is then passed to the regenerator.

With any cracking system the products are cooled and then separated into liquid and gas. An additional amount of gas is isolated on stabilization of cracked gasoline, i.e., during the distillation of volatile substances from it. It is just these gases that are a source of olefins used for organic synthesis.

1.2.3. Derivation and Concentration of Olefins

The gases obtained in various processes of cracking and pyrolysis differ by composition, which can be seen from Table 1.5. They may be divided into three groups.

1. Thermally and catalytically cracked gases containing many C_3 and C_4 hydrocarbons but little ethylene. These gases constitute

TABLE 1.5. The Composition of Cracked and Pyrolysis Gases (in percent by weight)

Component	Catalytic cracking	Pyrolysis of an ethane-propane mixture	Pyrolysis of gasoline
CH ₄	6-7	16-18	14-15
C ₂ H ₄	2.5-3.5	36-38	25-40
C ₂ H ₆	6-7	26-28	5-7
C ₃ H ₆	14-17	10-12	15-20
C ₃ H ₈	13-15	5-6	2-4
C ₄ H ₈	19-22	2-4	10-20
C ₄ H ₁₀	20-32	—	2-6
C ₄ H ₆	—	1-3	5-7
H ₂	0.7-0.9	1.5-2	0.4-0.6

an economical source of propylene and butylenes, the other components being delivered for pyrolysis or used for other purposes.

2. Gases from the pyrolysis of gaseous hydrocarbons which contain a small amount of higher fractions. These gases cannot serve as a source of butylenes; they are used to produce ethylene and propylene.

3. Gases from the pyrolysis of liquid petroleum products which contain considerable quantities of C₂—C₄ olefins.

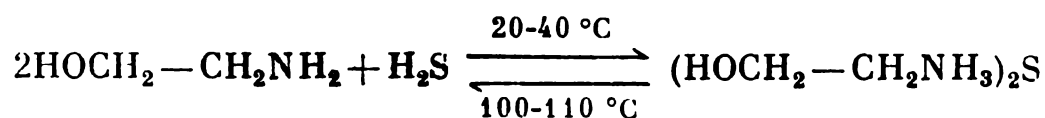
The cracked gases (the first group) are separated most frequently by the absorption-fractionation technique considered earlier for casinghead gases. This method is occasionally employed for the separation of pyrolysis gases, but at modern large-scale plants use is made of low-temperature fractionation, since it provides purer olefin fractions and less energy is required.

Preparation of Gases for Separation. Cracked and pyrolysis gases contain a number of impurities, which have to be removed at the preliminary stage. Some of these impurities cause the corrosion of the apparatus (H₂S), some solidify on cooling (CO₂, H₂O) and may lead to clogging of the apparatus, and others are close to olefins in boiling point and contaminate the fractions obtained (C₂H₂, methylacetylene). Besides, the gas contains the vapours of liquid (under ordinary conditions) hydrocarbons, which are of considerable value (benzene, amylenes).

The bulk of higher hydrocarbons and water are separated at the initial stage of gas compression. After this, at the intermediate and final stages of compression the gas is purified from the remaining impurities.

The method of purification of the gas from hydrogen sulphide and carbon dioxide is chosen, depending on the amount of impurities present. If there is a large amount of impurities, the most common

operation is the absorption with ethanolamines followed by the complete neutralization of acidic gases by caustic in scrubbers; with a small concentration of H_2S and CO_2 the gases are only washed with an aqueous solution of caustic soda. The purification by means of an aqueous solution of ethanolamines is based on the fact that these organic bases give with hydrogen sulphide and carbon dioxide salts, which are stable at low temperature and undergo dissociation on heating:



Therefore, in the desorber the ethanolamine can be regenerated and returned to the absorber. The final drying of the gas is effected with diethylene glycol or solid caustic, but most frequently it is done by means of aluminium oxide or zeolites, which adsorb moisture well.

For the gas to be purified from acetylene hydrocarbons, use is made of selective hydrogenation on heterogeneous catalysts which leaves the olefins untouched:



A palladium catalyst (on a support) and a nickel-cobalt-chromite catalyst which operate at $150-230^\circ\text{C}$ are suitable for this purpose. The reactive dienes may also be hydrogenated together with the acetylene. If the dienes are to be left unreacted, it is expedient to carry out the purification from acetylene after the C_4 fraction has been separated. This purification is often accomplished on the C_2-C_3 fractions obtained, which requires the addition of hydrogen to them.

Separation of the Pyrolysis Gas. There are numerous schemes for the separation of pyrolysis gases by low-temperature fractionation. They differ, first of all, by the fractions obtained and by their purity: commonly, the methane-hydrogen, ethylene, ethane, propylene and C_4 fractions are derived; not infrequently there is produced pure methane, the propylene fraction being separated from the propane present in it. Second, the sequence of separation of the fractions may differ; for instance, the C_3-C_4 hydrocarbons or the methane-hydrogen fraction is separated first. And, finally, use is made of different pressures (from 0.15 to 7 MPa), which determine in turn the cold gradient required to produce a reflux during fractional distillation.

The separation is most often effected at 3-4 MPa, in which case a temperature of -100°C is required for the methane-hydrogen fraction to be separated. It is achieved by means of the ethylene refrigeration cycle which can operate only in the presence of the propylene (less frequently, ammonia) refrigeration cycle. When compressed and cooled with water the propylene is capable of condensation and when throttled up to different pressures it can produce

a temperature ranging from 0 to -40°C . At such a temperature the compressed ethylene is condensed, as a result of which a temperature from -60 to -100°C is attained upon throttling to different pressures.

Because of the high cost of producing such a "cold", various economizing measures are taken at modern plants. First of all, the cold and pressure of the fractions obtained are utilized due to their throttling, expansion, the use of the thermal pump principle, etc. Wide use is also made of the stepwise cooling by agents with different temperature gradients, which is also employed to produce a reflux in so-called sectioned fractionating columns divided into two or more sections with their separate reflux condensers, of which only the top one operates at the lowest temperature. The gas and condensate are introduced separately along the height of the columns at the points corresponding to their composition, etc. As a result of these measures, the energy consumption for the separation of the gas has been reduced and the olefin fractions produced have become less costly; the latter result is achieved also by introducing improvements at the pyrolysis stage and by enlarging the plants.

One of the present-day schemes of separation of the gases produced in the pyrolysis of gasoline is shown in Fig. 1.11. The gas from the pyrolysis unit is successively compressed in the five stages of turbocompressor 1 and passed from each of these into water cooler 2 and separator 3, where it is separated from the condensate (water and organic compounds). For the heavier hydrocarbons to be separated more efficiently the condensate from the next compression stage is throttled and returned to the separator of the preceding stage. As a result, a fractionation effect is created and the hydrocarbons that are liquid under ordinary conditions accumulate in the condensate after the first stage of the compressor. These hydrocarbons are separated from the soluble gases in stripper 4. The resulting pyrocondensate is withdrawn for processing and the gases are returned to the suction line of the first stage of the compressor.

After the third compression stage the gas is purified from acidic impurities. The purification is effected with an aqueous caustic soda solution circulating through packed scrubber 5. The gas is then compressed to a final pressure of 3.5-4 MPa. The condensate formed at the fifth stage of the compressor is throttled and returned to the fourth-stage separator, the condensate from which is led to stripper 6. The dissolved gas is distilled off there and returned for compression to the fourth stage of the compressor. The still liquid of column 6 consists mainly of $\text{C}_4 + \text{C}_5$ hydrocarbons; to separate these hydrocarbons from the C_3 fraction the light pyrocondensate is then passed to depropanizer 20, where it is processed together with the $\text{C}_3 + \text{C}_4$ fraction isolated on deep cooling.

After the higher hydrocarbons are separated the gas is passed

osition of the vapour and liquid) plates of fractionating column 13, which is called the demethanizer. Its function is to separate the methane-hydrogen fraction from the heavier hydrocarbons collected in the column still. Methane is a difficultly liquefiable gas and, besides, it is diluted with hydrogen, which lowers its condensation temperature even more strongly. Therefore, in order to produce reflux in the demethanizer, the deepest cooling is required and refrigeration in the reflux condenser is carried out mainly by the vaporization of the liquid ethylene from the refrigeration cycle at atmospheric pressure and -100°C . For a partial replacement of this cold the methane-hydrogen fraction isolated is throttled up to 0.5–0.6 MPa and its cold is used in the upper fractionating column of the demethanizer.

The still liquid of demethanizer 13 consists mainly of C_2 – C_4 hydrocarbons. The next operation is to separate the C_2 and C_3 hydrocarbons, which is effected in fractionating column 14 called the deethanizer. The ordinary pressure in it is 2.5 MPa and the temperature at the top is about -10°C ; therefore, for a reflux to be produced, cooling by the propylene refrigeration cycle is required (the propylene is evaporated at a certain pressure that can provide the required boiling point). The mixture of ethylene and ethane with impurities of acetylene and small amounts of methane and propylene is withdrawn from the top of column 14. This fraction is led to a unit where it is subjected to hydrorefining to be freed from acetylene. It is heated in heat exchanger 15 by the heat of the recycle stream and then in steam heater 16, following which a small amount of hydrogen is added and the fraction is hydrogenated in contact apparatus 17 over a heterogeneous catalyst.

The purified fraction is cooled by water in cooler 18 and then by the cold fraction in heat exchanger 15, after which it is passed to fractionating column 19 called the ethylene column. The function of this column is to separate the ethylene and ethane and to simultaneously purify the ethylene from the methane and the hydrogen introduced during hydrorefining.

Column 19 usually operates under 2–2.3 MPa pressure with the temperature at the top ranging from -30 to -35°C , which is achieved by cooling the reflux condenser through the evaporation of the liquid propylene from the refrigeration cycle. The hydrogen admixed with methane and ethylene is removed from the top of the column and returned to the corresponding stage of compression of the gas feed. The liquid ethylene is withdrawn from one of the top plates of column 19. Sometimes it is stored in the liquid state, in which case it is led directly to storage or transportation tanks. More often, gaseous ethylene is required; it may be used at different pressures. Depending on whether it is in the liquid or gaseous state, the cold of the ethylene fraction is utilized in various ways (for example, in the same way

as the ethane fraction). In the still of column 19 the liquid ethane fraction is collected, which is throttled and its cold used as described above.

The still liquid of deethanizer 14 is led for fractional distillation to column 20 called the depropanizer. The light condensate from the gas compression stage which also contains C_3 — C_5 hydrocarbons is also passed to column 20. In the column the propane-propylene fraction is distilled off at a pressure of about 2 MPa, for which purpose it is sufficient that the reflux condenser is cooled by water. This fraction is derived and stored in the liquid form, but, depending on the pressure required in subsequent syntheses, it can be throttled and its cold used for various purposes. The $C_4 + C_5$ fraction is collected in the still of the depropanizer and is subjected to additional separation into the butylene and amylene fractions in column 21.

Concentration and Separation of Olefin Fractions. The ethylene fraction isolated during the separation of the pyrolysis gases often contains up to 2-3 percent of methane and ethane and also up to 1-2 percent of acetylene if it has not been purified from the ethylene fraction. At modern plants the quality of ethylene is much higher, since a purity of 99.9 percent and higher is needed for its polymerization to polyethylene.

Depending on the source, the propylene fraction may contain various amounts of propylene and propane. For example, if it is derived from cracked gases, the content of propylene is only 30-40 percent by volume, and in the pyrolysis of hydrocarbon gases it is 60-80 percent by volume; in the pyrolysis of gasoline up to 90-95 percent by volume of propylene are contained in the propylene fraction. The other components present include C_2 and C_4 hydrocarbons (0.2-2 and 0.3-2 percent by volume, respectively) and also methylacetylene and propadiene (0.5-2 percent by volume each) if no hydrorefining has been carried out. Not infrequently, these propylene fractions are used for syntheses without being additionally purified, which refers especially to more concentrated fractions derived from the pyrolysis gases. For a number of syntheses, however, it is expedient to concentrate propylene fractions, the major proportion of propane being separated by fractional distillation. Because of the closeness of its boiling point to that of propylene ($\Delta t = 5.5^\circ\text{C}$) a column with 100-200 trays and a reflux ratio of about 10 are required. During fractional distillation methylacetylene together with propadiene also pass into the propane fraction. High-purity propylene (99.9 percent pure) is also derived; it is needed as a raw material for polypropylene production.

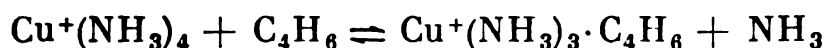
Depending on the source, the butylene fractions may differ not only in relative content of the butylenes and butanes but also in the ratio of their various isomers and also in the content of 1,3-butadiene (in percent by weight):

Component	Catalytic cracking	Pyrolysis
<i>n</i> -C ₄ H ₁₀	10-20	5-10
<i>iso</i> -C ₄ H ₁₀	35-50	5-10
<i>n</i> -C ₄ H ₈	25-40	30-40
<i>iso</i> -C ₄ H ₈	5-10	20-30
• C ₄ H ₆	—	20-30

Apart from these components, the fraction also contains C₃ hydrocarbons (0.5-2 percent by weight) and C₅ hydrocarbons (0.5-1.5 percent by weight).

The separation of the butylene fraction by means of ordinary fractional distillation is impossible because of its components having close volatilities. Therefore, one has to resort to special techniques based on extractive distillation, chemisorption or on the differences in reactivity of olefins.

In the processing of the pyrolysis C₄ fraction, the derivation of 1,3-butadiene is frequently accomplished by chemisorption with aqueous solutions of ammonia complexes of cuprous acetate:



As can be seen from Table 1.4, such complexes with butadiene are more stable than the corresponding complexes with olefins and when the fraction is treated with an absorbent solution at -10 to 0°C , 1,3-butadiene is mainly extracted. Upon heating up to 40°C there occurs the desorption of the bound olefins with a certain proportion of the butadiene; at $70-75^\circ\text{C}$ pure butadiene is isolated and the absorbent solution is returned to sorption after it is cooled. The operation is carried out in a counterflow cascade of units with stirrers; each of the units is equipped with a separator and a pump. The fresh absorbent solution is fed to the first unit and the butylene fraction to the last one, which creates the most favourable conditions for the sorption of the diluted fraction by the fresh absorbent solution, the concentrated fraction being absorbed by the saturated solution.

At modern plants the chemisorption is effected in several extraction columns, in which the liquid fraction and the absorbent solution move in counterflow due to the difference in their density (Fig. 1.12). The cooled sorbent is passed to the top of extractor 1 and moved downwards through all the three units. The feed C₄ fraction is passed to the middle of the third extractor; being lighter, it moves upwards and is pumped from one column to another. The C₄ fraction (C₄H₁₀ + C₄H₈) freed from the butadiene is withdrawn from the top of extractor 1, which functions as a separator. The saturated solution from the bottom of extractor 3 moves to stripper 4, where the entrained olefins are distilled off at 40°C . Since these olefins contain a large amount of butadiene, they are returned for sorption to the bottom of column 3. The solution from the still of column 4 is led to strip-

per 5, where the butadiene is desorbed due to heating and the regenerated sorbent is chilled in cooler 6 and returned to the extractors.

The technique that has recently found an ever increasing application for the derivation of 1,3-butadiene is extractive distillation. The extractants that have an advantage over furfural are acetonitrile and N-methylpyrrolidone, in whose presence the difference in relative

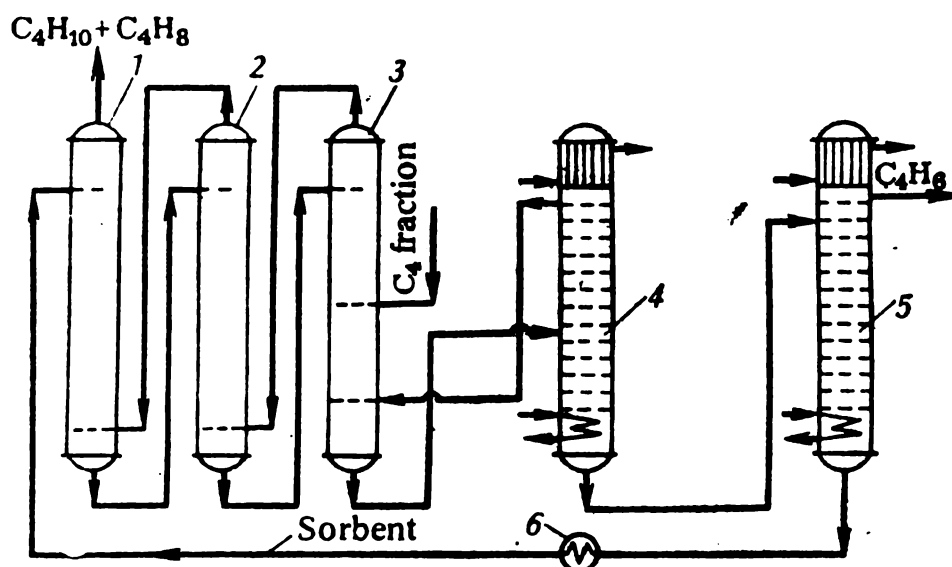
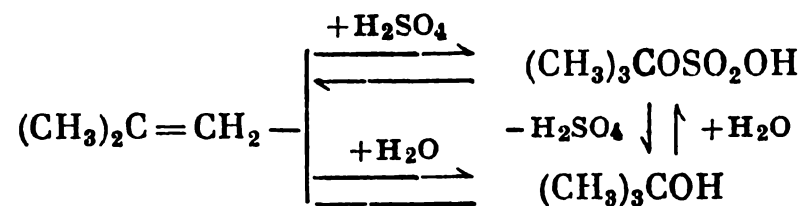


Fig. 1.12. Flow diagram for isolation of 1,3-butadiene from the C_4 fraction by chemisorption:

1, 2, 3—extraction columns; 4, 5—strippers; 6—cooler.

volatility between 1,3-butadiene and olefins increases (Table 1.4); the 1,3-butadiene can immediately be separated from the other components. The isobutylene has, however, to be extracted by chemical means, of which the sulphuric-acid method has found the widest application. It is based on the fact that the more reactive isobutylene interacts with 40- to 60-percent H_2SO_4 , with which the other olefins do not react. At a sufficiently low temperature there are formed *tert*-butylsulphuric acid and *tert*-butanol which decompose to isobutylene when the solution is heated:



The by-products formed in this reaction are the lower polymers of isobutylene.

The flowchart of separation of the C_4 fraction of gasoline pyrolysis by extractive distillation is shown in Fig. 1.13. The C_4 fraction is fed to the middle part of column 1 and acetonitrile is introduced into the top of the column. The solution from the still is passed into stripper 2, where the 1,3-butadiene is distilled off and the extractant is regenerated and returned to column 1. The mixture of butylenes

and butanes that has not been absorbed is moved to unit 3 for the chemisorption of the isobutylene, after which the residue is passed to column 4 for extractive distillation. The butanes are removed

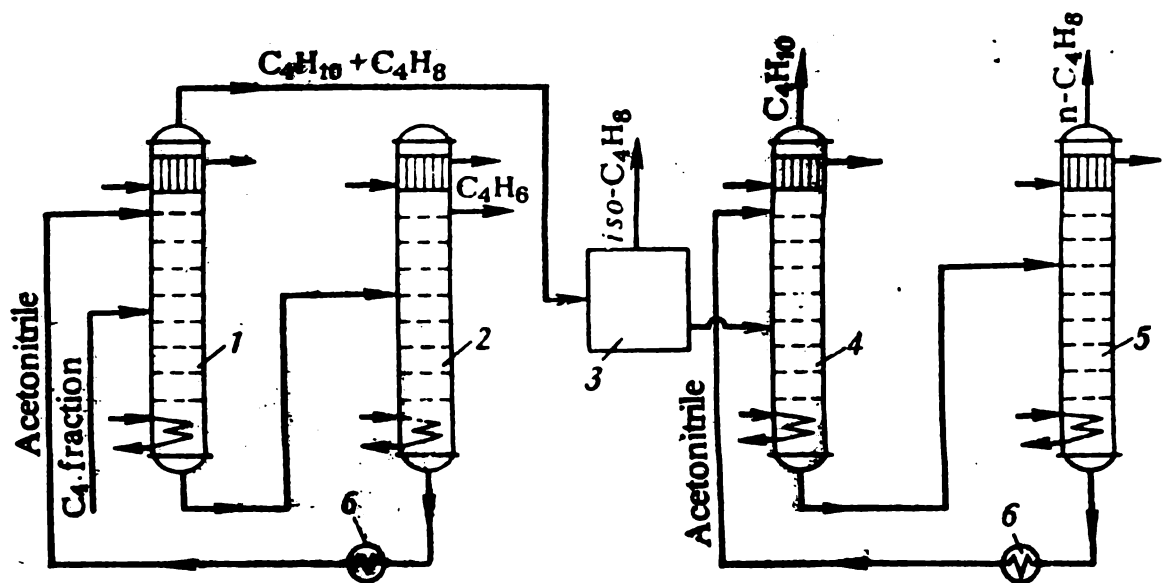


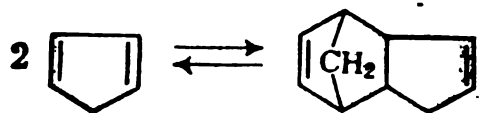
Fig. 1.13. Flow diagram for separation of the C₄ fraction by extractive distillation:
 4—extractive distillation columns; 2, 5—stripping columns; 3— isobutylene chemisorption unit; 6—coolers.

from the top of the column and can be subjected to additional fractionation for the production of individual *n*-butane and isobutane. The *n*-butylenes are stripped off in column 5 from the extractant, which is returned to column 4.

The amylene fraction has a more complex composition, which is approximately as follows (in percent by weight):

	Catalytic cracking	Gasoline pyrolysis
<i>n</i> -Pentane	12	26
Isopentane	60	24
<i>n</i> -Pentane	12	} 12
Isopentane	16	
Cyclopentane	—	1-2
Pentadiene	—	9
Isoprene	—	13
Cyclopentadiene	—	8-12

The most important of these compounds are isopentene, isoprene and cyclopentadiene and also isopentane. Cyclopentadiene is derived by way of its dimerization:



The amylene fraction is kept under pressure and at 100-120 °C, allowing which the other hydrocarbons are distilled off from the

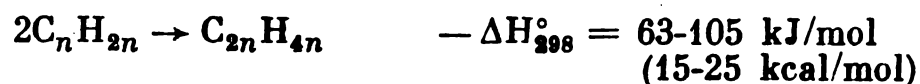
higher-boiling dimer. This dimer can then be depolymerized at 200 °C to give cyclopentadiene. This hydrocarbon and its dimer are valuable raw materials for a number of syntheses.

The isoprene from the C₅ fraction of gasoline pyrolysis is derived only by extractive distillation combined with the partial distillation of the impurities and with the fractionation of the crude fraction, since the chemisorption by means of cuprammonium solutions is not sufficiently selective in this particular case.

1.2.4. Production of Olefins by Their Interconversion Reactions

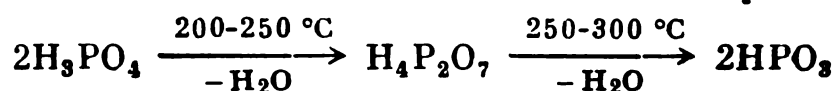
1.2.4.1. Acid Oligomerization of Olefins

The polymerization of olefins is an equilibrium reaction, being the reverse of their cracking:



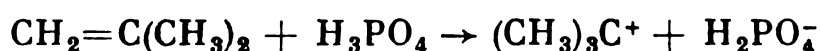
Accordingly, in contrast to the cracking of olefins (see Fig. 1.5, curve 1), the polymerization is thermodynamically feasible only at a temperature below 500 °C. An increase in pressure favours polymerization, since it proceeds with a decrease in volume. The equilibrium of the process depends to a considerable extent on the structure of the olefin and of its lower polymers. For instance, for strongly branched hydrocarbons the thermodynamic relations for polymerization are less favourable, as a result of which diisobutylene undergoes depolymerization even at 120-150 °C.

Low-molecular-weight polymers (oligomers) are usually obtained by using an elevated temperature and acid-type catalysts. The heterogeneous catalyst developed by Ipatiev has assumed practical importance. It is prepared by impregnating kieselguhr (diatomaceous earth), asbestos or other materials with orthophosphoric acid. At 200-300 °C the acid is dehydrated, as a result of which pyro- and meta-phosphoric acids are obtained:

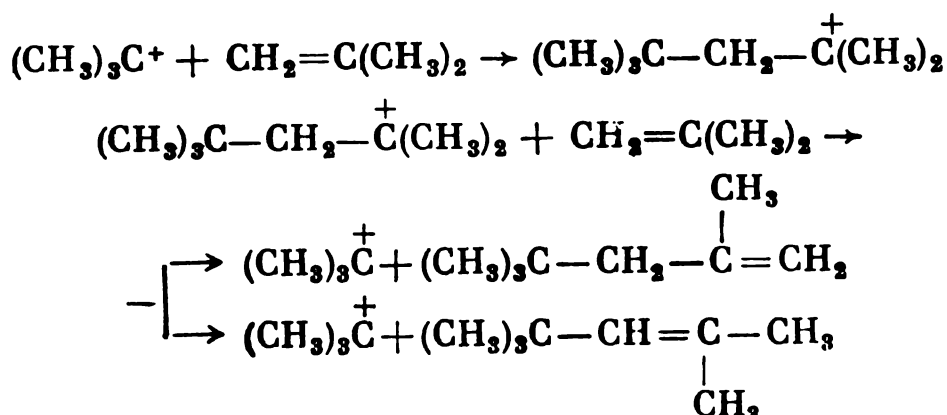


Catalytic activity is displayed only by ortho- and pyrophosphoric acids; in order to avoid their strong dehydration, steam has to be added constantly to the reaction mass because it shifts the reaction equilibrium to the favourable side.

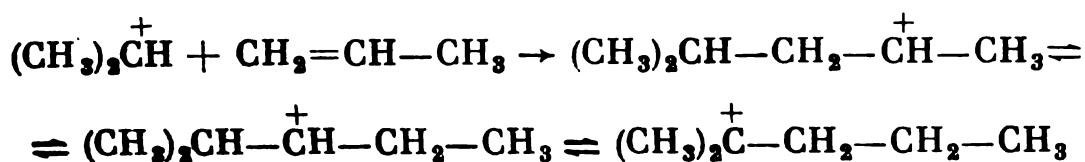
The polymerization with acid catalysts proceeds by an ionic mechanism with the intermediate formation of carbonium ions as a result of the addition to the olefin of the proton given off by the acid:



The further process occurs in a stepwise manner by way of the successive addition of carbonium ions at the double bond of the olefin with a proton being transferred to the olefin or another proton acceptor (H_2O , H_2PO_4^- , etc.). The composition and structure of the dimers of isobutylene (80 percent of 2,4,4-trimethyl-1-pentene and 20 percent of 2,4,4-trimethyl-2-pentene) allow one to assume that they are formed according to the following scheme:

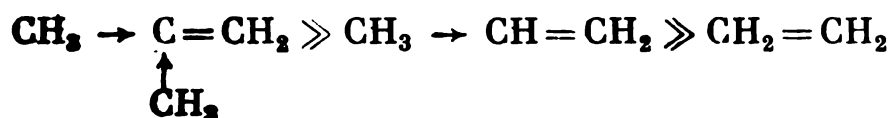


The structure of the polymers of *n*-olefins is more complex, since the secondary carbonium ions that are formed as intermediates are liable to isomerization:



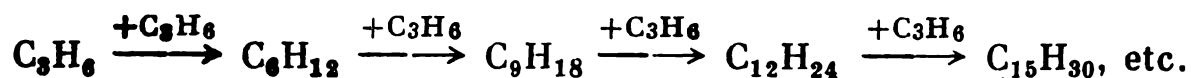
Upon further reaction with the olefin and detachment of a proton there are formed numerous isomers, which include the following hydrocarbons: $\text{CR}_2=\text{CHR}$ (about 45 percent), $\text{CR}_2=\text{CR}_2$ (about 15 percent) and $\text{CHR}=\text{CHR}$ (about 30 percent).

During the acid polymerization the reactivity of olefins varies in the usual manner, this being accounted for by the inductive effect of the alkyl substituents:



Because of this, for isobutylene to be polymerized milder conditions are required than for propylene and *n*-butylenes, whereas ethylene is polymerized with great difficulty.

The acid polymerization of olefins is kinetically a consecutive process leading to the formation of a mixture of products with different degrees of polymerization:



The composition of the products is controlled by the degree of conversion of the starting olefin; if the end product is propylene tetramer, the dimer and trimer are returned to polymerization.

The oligomerization of olefins involves some side reactions, especially when the temperature is increased: there are formed paraffins, naphthenes, aromatic hydrocarbons, and tarry condensation products. As a result of the splitting of the intermediate carbonium ions and subsequent co-oligomerization, there are formed olefins with a number of carbon atoms which is not a multiple of that of the starting olefin. In order to avoid the side reactions mentioned the polymerization of olefins should be carried out at the lowest temperature possible, at which a sufficient rate of the basic process can nevertheless be achieved.

Technology of the Acid Polymerization of Olefins. Propylene, isobutylene, mixtures of butylenes with propylene and of butylenes with amylenes are polymerized industrially in the presence of a solid phosphoric-acid catalyst for the manufacture of the trimer or tetramer of propylene (isononene and isododecene), diisobutylene, a copolymer of propylene and *n*-butylene (isoheptene), etc.

The C_3 and C_4 hydrocarbon fractions derived from the cracker gases (propane-propylene and butane-butylene fractions) are usually subjected to acid polymerization reactions.

As has been pointed out earlier, the polymerization is influenced favourably by an increase in pressure. This is accounted for not only by the thermodynamic factors but also by a considerable acceleration of the process and by the possibility of working without regeneration of the catalyst. At a low pressure, the higher polymerization and resinification products are gradually sorbed on the catalyst; when the pressure is increased, part of the polymerization products undergoes condensation, entraining compounds that deactivate the catalyst into the liquid phase. The operations are usually carried out at 3-6 MPa, which provides a long service life of the catalyst without regeneration.

When the process is carried out on an industrial scale, an important factor is the necessity of maintaining an optimal temperature with a high exothermicity of the reaction (the temperature range required for ethylene is 320-350 °C and propylene is polymerized at 180-240 °C and isobutylene at 130-170 °C). The heat is partly accumulated by the excess olefin (and paraffin if its content in the fraction is considerable). The major part of heat has, however, to be removed because of the external heat exchange, the process being carried out in a tubular reactor, in the pipes of which there is present a catalyst and the reaction mixture is moving. Refrigeration is effected using the coolant circulating in the intertubular space; it is expedient to use the boiling condensate as a heat carrier by generating steam of the appropriate pressure.

The unconverted olefin (together with the corresponding paraffin if it was present in the feedstock) is first distilled off from the reaction products and returned to the reaction. Then, the lower oligomers

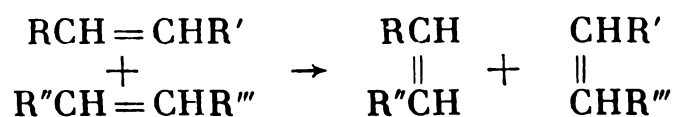
are separated and, if they are not the end products, they are recycled. And, finally, the desired oligomer is distilled off; it contains a small amount of lower and higher oligomers. Sometimes, the final products are two oligomers, say, a trimer and a tetramer of propylene. The residue from the fractional distillation consists of higher oligomers, whose amount is usually reduced to a minimum.

When these oligomers are put to practical applications, one should keep in mind that they have a highly branched structure, which is responsible for the poor biodegradability of the compounds synthesized from them. Their application is therefore limited to areas where the biodegradability of the product is not important.

Apart from the technique described above, there is also another method of oligomerization of olefins which consists of the organoaluminum synthesis of the higher alpha-olefins. It will be considered in Chapter 4.

2.4.2. Disproportionation of Olefins

The recent discovery of the reaction of disproportionation (metathesis) of olefins, which proceeds according to the general equation



provoked great interest. The unusual manner in which the double bond is broken and formed is evidently due to the intermediate formation of adducts of the type of the carbenes $\text{R}_2\text{C:}$ and their subsequent conversion.

This process is of practical importance mainly for the disproportionation of propylene to ethylene and *n*-butylene:



and of a mixture of propylene and isobutylene to ethylene and 2-methyl-2-butene:



The *n*-butylene and 2-methyl-2-butene obtained can further be converted, respectively, to butadiene and isoprene. These reactions are reversible and practically exhibit no heat effect. Because of this fact, the equilibrium degree of conversion depends little on temperature, being equal to 50-55 percent for the disproportionation of propylene.

The disproportionation reactions proceed in the presence of numerous homogeneous and heterogeneous catalysts, the most effective among which are molybdenum and tungsten oxides supported on Al_2O_3 or SiO_2 . Their high activity is achieved at 150-400 °C; in order to increase the capacity use is made of a pressure of 1-4 MPa.

The process is carried out in an adiabatic reactor with a continuous catalyst bed, which is periodically regenerated by burning off the coke with air at 500 °C. Apart from the basic process, there occur side reactions of isomerization and cracking of the olefins and also of disproportionation involving the products formed. The selectivity is, however, high, amounting to 95-97 percent with the degree of conversion of propylene being 40-45 percent. The reaction gases are separated by fractional distillation under pressure, the unconverted propylene being returned to the reaction.

The disproportionation of propylene has been accomplished on an industrial scale (the *Triolefin* process), but it has not found wide application.

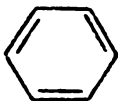
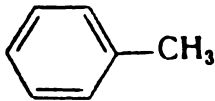
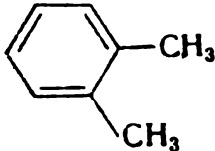
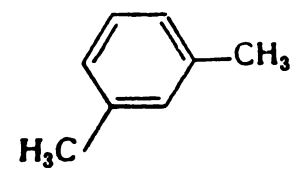

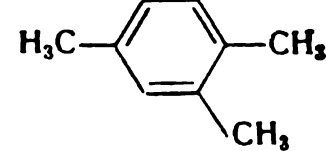
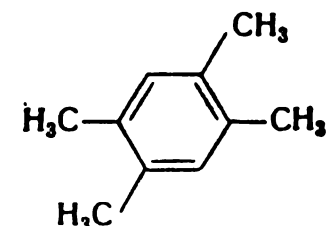
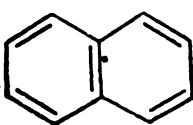
1.3. Aromatic Hydrocarbons

As raw materials for organic synthesis, aromatic hydrocarbons rank second after olefins. Of the aromatic compounds derived from natural sources the most important are benzene and xylenes, whose annual production in the United States amounts, respectively, to 5.5 and 2.5 million tons. Naphthalene, toluene, pseudocumene and durene are used on a smaller scale; the last two compounds are partly produced by synthetic means. Some of their properties are given in Table 1.6. The boiling points of the xylene isomers are very close and they can be separated only partly, and this can be achieved only by a clear-cut fractional distillation (this refers also to isomeric tri- and tetramethylbenzenes). *n*-Xylene and durene melt at higher temperatures than other isomers, a fact which is used for their separation from mixtures by crystallization. This method is also employed for the separation of naphthalene.

The presence of a system of aromatic bonds confers on aromatic hydrocarbons a higher ability to be sorbed than is the case with other hydrocarbons, especially with paraffins and naphthenes. Aromatic hydrocarbons dissolve well in polar liquids, such as liquid sulphurous anhydride, diethylene glycol, phenol, in which hydrocarbons of other classes dissolve with difficulty. They are well sorbed by solid adsorbents (activated charcoal, silicagel). These properties of aromatic hydrocarbons are used in industry for their separation by extraction, extractive distillation and adsorption.

As can be seen from Table 1.6, benzene, toluene and xylenes have a low flash temperature and therefore present fire hazard. In their toxic properties, aromatic hydrocarbons by far exceed hydrocarbons of other classes and are blood poisons, which disturb the medullary hematosis system. Because of this, the permissible maximum concentration (PMC) on industrial premises is 20 mg/m³ for benzene and 50 mg/m³ for toluene and xylenes.

TABLE 1.6. Properties of Aromatic Hydrocarbons

Hydrocarbon	Formula	Boiling point at atmos- pheric pres- sure, °C	Melting point, °C	Flash tempe- rature, °C
Benzene		80.1	+5.5	-14
Toluene		110.6	-95.0	+5
Xylene		144.4	-25.2	+29
m-Xylene		139.1	-47.9	+29
p-Xylene		138.3	+13.3	+29
Pseudocumene		169.3	-43.8	—
Triene		196.8	+79.2	—
Naphthalene		218.0	+80.3	—

The aromatic hydrocarbons are mainly produced by the aromatization of raw materials, namely by pyrolysis and reforming of petroleum products and coal coking.

3.1. Aromatization of Petroleum Products

3.1.1. Pyrolysis Products as a Source of Aromatic Hydrocarbons

It has been said earlier that the pyrolysis of petroleum products with the purpose of producing lower olefins involves the aromatization of straight-chain hydrocarbons. As a result, in liquid pyrolysis

products (in the pyrocondensate and tars) there are accumulated large amounts of aromatic hydrocarbons, which can be derived from them.

As we have seen above, the yield of tar falls off in the pyrolysis of a lighter raw material, with increasing temperature and contact

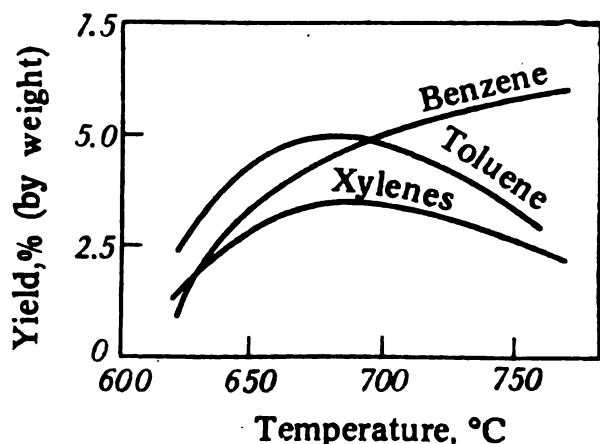


Fig. 1.14. Temperature dependence of the yield of aromatic hydrocarbons in pyrolysis of liquid petroleum products.

time. An increase in temperature and contact time leads to an increase in the degree of aromatization of the pyrolysis tar, i.e., in the content of aromatic compounds. As a result, their yield as percentage of feedstock, other conditions being equal, passes through a maximum, depending both on temperature (Fig. 1.14) and on the contact time. In modern gasoline pyrolysis plants, the overall yield of tar achieved under severe conditions is 20-25 percent (by weight), the tar containing 85-95 percent of aromatic

substances. In the pyrolysis of C_3 — C_4 hydrocarbon gases the yield of tar having nearly the same composition falls to 5-8 percent. Here, just as in not too large gasoline pyrolysis plants, it is expedient to centralize the tar processing in several specialized plants.

The liquid pyrolysis products are subjected to primary processing and separated into four fractions: (1) the so-called head fraction containing mainly C_5 paraffins and olefins, the uses of which have been considered above; (2) the "light" oil (75-180 °C), which consists mainly of monocyclic aromatic compounds admixed with olefins and paraffins; (3) the "middle" oil (180-300 °C); (4) the residue used for the production of ash-free coke. The methods of separation of aromatic compounds from these fractions will be considered in Sec. 1.3.3.

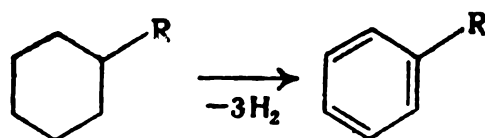
1.3.1.2. Catalytic Reforming

Reforming was originally designed to upgrade gasoline quality (to raise the octane number of straight-run gasoline). This process was subsequently employed for the production of aromatic hydrocarbons.

In contrast to catalytic cracking over aluminosilicates, in catalytic reforming use is made of bifunctional catalysts. The most important of these catalysts are platinum on highly porous aluminium oxide (*platforming*) and a platinum-rhenium catalyst on an acid-type support (a recent development, the process being called *rheniforming*).

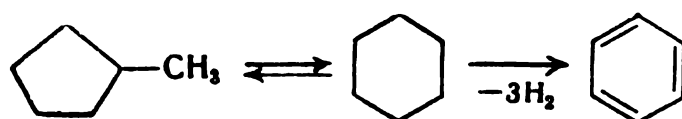
The two processes are accomplished at 470-540 °C under pressure in the presence of hydrogen.

The chemical transformations involved in catalytic reforming are determined by the bifunctionality of the catalyst. The acidic centres are predominantly the sites of the isomerization of paraffins to isoparaffins and of five-membered naphthenes to homologues of cyclohexane. On the other hand, over a metal (Pt or Pt + Re) there take place a number of homolytic conversions, of which the dehydrogenation of six-membered naphthenes contained in the feed fraction has become important:



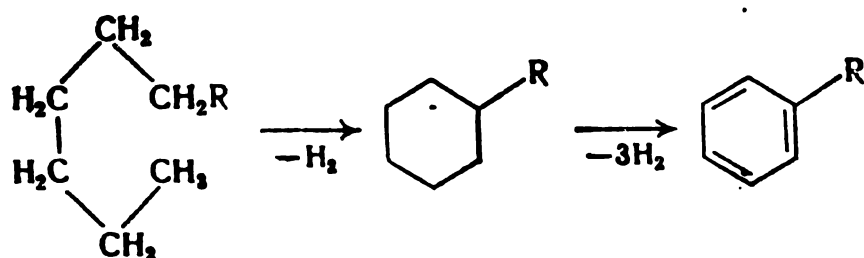
As is seen from Fig. 1.4, this reaction is thermodynamically feasible even at 520-570 K (250-300 °C), its equilibrium being strongly shifted to the right with a further rise in temperature.

The five-membered naphthenes are first converted to cyclohexane and its homologues and upon further dehydrogenation they also give aromatics:



The thermodynamic data show that the equilibrium of this isomerization reaction at a high temperature is unfavourable for the formation of cyclohexane. However, because of the subsequent dehydrogenation to aromatics, the six-membered naphthenes are continuously removed from the system, which provides a high degree of conversion of the homologues of cyclopentane.

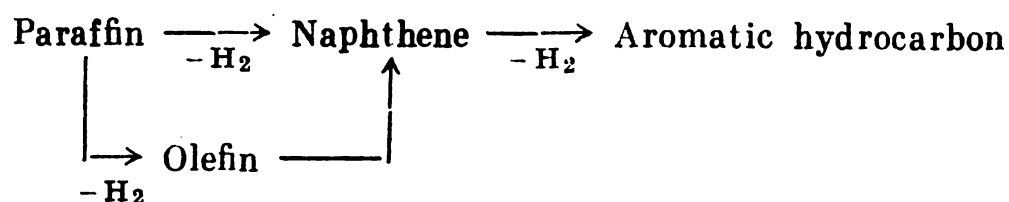
When the reforming conditions become severe, an ever increasing role in the formation of cyclic compounds is played by the dehydrocyclization of paraffins:



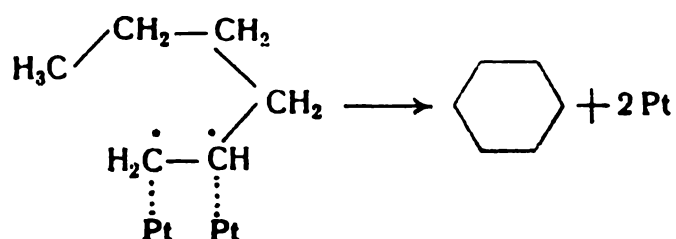
Five-membered naphthenes are formed in a lesser amount; they are converted into aromatic hydrocarbons by the route considered above.

In accounting for the mechanism of dehydrocyclization it is presumed that (1) the paraffin undergoes direct dehydrocyclization to

a naphthene, which is then dehydrogenated to an aromatic hydrocarbon or (2) the paraffin is dehydrogenated to an olefin, which then undergoes cyclization:



When a paraffin or olefin molecule is adsorbed on two adjacent active centres of the catalyst, there are formed intermediate adducts of the free-radical type, which are then closed into a ring:



Isoparaffins, whose main chain consists of five carbon atoms, are also capable of aromatization. This may be accounted for by their preliminary isomerization to paraffins with a longer chain or by the closure of the five-membered ring with subsequent isomerization to a six-membered ring.

Apart from the reactions considered above, which are designed to produce the end products in reforming processes, there also occur side reactions, which are often undesirable. For example, higher hydrocarbons are partially cracked with the formation of lower gaseous olefins and paraffins. In the presence of hydrogenating catalysts (Pt) the olefins become saturated with hydrogen to give paraffins. Therefore, in contrast to cracker gases, the reforming gases consist almost exclusively of paraffins strongly diluted with hydrogen.

Another undesirable reaction is the *dehydrocondensation* of aromatic hydrocarbons with the formation of polycyclic and condensed compounds. Its further progress leads to a considerable formation of coke, which is deposited on the catalyst surface and deactivates it. Since the dehydrocondensation reaction is reversible, the reforming effected under hydrogen pressure prevents extreme coking and prolongs the service life of the catalyst.

The role of the above-mentioned reactions in the overall balance of the reforming process depends on the fractional and group composition of the raw material, temperature, hydrogen pressure and other factors. It has been found that dehydrocyclization proceeds more readily with branched-chain paraffins and is speeded up with increasing number of carbon atoms in the main chain. The hydrogen pressure not only prevents the formation of coke but also favours the isomerization of paraffins and the hydrogenolysis of naphthenes and

paraffins, the dehydrocyclization being however slowed down. An increase in temperature speeds up all reactions, especially the cracking of liquid hydrocarbons, in which case gaseous products are formed. An appropriate choice of the process parameters can provide the most favourable reforming conditions for a given type of feedstock.

Technology of Catalytic Reforming. At present the reforming process is employed on an industrial scale to achieve two purposes: to raise the octane number of motor fuels and to produce individual aromatic hydrocarbons. The feedstock in the first case is the ligroin fraction or heavy straight-run gasolines, whose octane number is increased, as a result of reforming, from 55-60 to 80-90. In the second case, the feedstocks for the reforming process are the narrower fractions of petroleum containing paraffins and naphthenes with the same number of carbon atoms as the end aromatic hydrocarbon. When benzene, toluene and xylenes are to be produced, the feedstocks are fractions that boil in the following ranges: from 60 to 85 °C for benzene, from 85 to 105-110 °C for toluene and from 110 to 130-135 °C for the xylenes. In order to produce benzene, more severe reforming conditions are required than for the formation of its homologues.

Owing to hydrogen pressure the reforming catalyst, as has been pointed out above, can operate for a long period of time without considerable coking and deactivation. At 3.5-5 MPa, when coke deposition is nearly excluded, the catalyst is not regenerated at all (the nonregenerative process), and after 1-2 years of service the platinum is extracted from the spent catalyst and used for the preparation of another catalyst. A disadvantage of this system is the low degree of aromatization of the feedstock. The scheme involving the regeneration of the catalyst (*ultraforming*) employs a lower hydrogen pressure (1.5-2 MPa), the coke being burned off the catalyst every 5-7 days.

In *rheniforming*, the catalyst is more stable and is capable of operating at a lower pressure (1 MPa) and high loads, providing an increased degree of aromatization of the feedstock. More than 90 percent of naphthenes and about 50 percent of paraffins are converted into aromatic hydrocarbons.

The catalyst used for reforming is more susceptible to poisoning by sulphur compounds, the sensitivity being the higher the lower the hydrogen pressure. It is for this reason that gasoline or another narrow straight-run fraction of sour crude oil is preliminarily purified from sulphur compounds, usually by hydrogenation over catalysts that are stable towards sulphur (cobalt, tungsten and molybdenum oxides or sulphides or their mixtures):



The flow diagram of the platforming process is given in Fig. 1.15. The feed petroleum fraction is heated in heat exchanger 5, mixed with hydrogen and then heated in tubular furnace 6 to a temperature

required for purification from sulphur. The hydrotreating is effected in contact unit 4 over a catalyst stable to sulphur compounds. The hot gases from unit 4 give off their heat to the feed fraction in heat exchanger 5 and cooled with water (and partly condensed) in cooler 2. In separator 1 the condensate is separated from H_2 and H_2S and run by pump 3 to the reforming stage.

Before the feedstock enters heat exchanger 10 it is mixed with the circulating hydrogen and then heated in heat exchanger 10 and

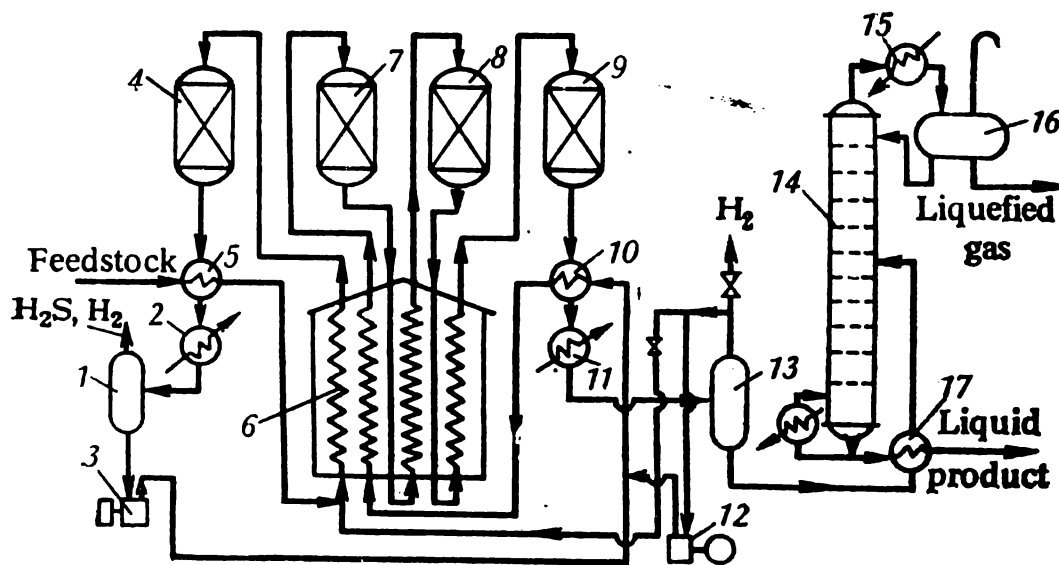


Fig. 1.15. Flow diagram of the platforming process:

1, 13—separators; 2, 11—coolers; 3—pump; 4—hydrotreating reactor; 5, 10, 17—heat exchangers; 6—tubular furnace; 7, 8, 9—reforming reactors; 12—circulation compressor; 14—stabilizing column; 15—condenser; 16—collector.

in tubular furnace 6. Platforming is accomplished in adiabatic-type reactors 7, 8 and 9. Because of the high endothermicity of the process, the reaction mass from reactors 7 and 8 has to be heated in furnace 6. In the last contact unit 9 platforming is completed. The heat of the hot gases is used in heat exchanger 10 to heat the mixture that goes to reforming and then the gases are cooled in cooler 11. The resulting condensate is separated from hydrogen in separator 13 and run for stabilization.

The hydrogen (admixed with the lower paraffins) from separator 13 is split into three streams. One stream is run by means of circulation compressor 12 to be mixed with the purified petroleum fraction sent to reforming; the second is blended with the feed fraction and led to hydrotreating, the remainder being withdrawn from the system.

The stabilization of the liquid reforming product consists of the distillation of the lower hydrocarbons (C_4H_{10} , C_3H_8 , and partly of C_2H_6) that have dissolved in it at elevated pressure. The condensate from separator 13 is heated in heat exchanger 17 and run to stabilizing column 14. In this column the lower hydrocarbons are distilled off, their vapours are condensed in condenser 15, and the condensate runs down into collector 16. Part of it is led to the upper plate of the

column as a reflux, the remainder being removed from the system as liquefied gas. The stabilized product from the still of column 14 gives off its heat to the condensate in heat exchanger 17 and is passed on for further refining. The derivation of aromatic hydrocarbons from the liquid reforming products will be considered in Sec. 1.3.3.

1.3.2. Coal Coking

This process is designed to produce metallurgical coke. Special-grade coal (coking coal) or a mixture of coals (coal blends) is heated in the absence of air up to about 1000 °C in special coke ovens.

Coking is accompanied by deep chemical transformations of the organic mass of coals, in which, just as in the thermal cracking of petroleum products, there are formed coke, liquid coking products and gas. Coal contains less hydrogen than crude oil, and therefore the coke yield is very high (75-80 percent), and the yield of liquid products is insignificant (4-5 percent).

The organic coal mass is known to consist of hydrocarbons, and oxygen-, sulphur-, and nitrogen-containing compounds of complex structure. The last three classes of compounds decompose on coking with the liberation of water, carbon oxides, hydrogen sulphide, carbon disulphide, ammonia and also of lower oxygen-, sulphur- and nitrogen-containing organic compounds (phenol, thiophene, pyridine and their homologues) and their more complex condensed-ring analogues. The hydrocarbons originally present in coal and derived upon decomposition of compounds of other classes undergo deep transformations. These transformations are based on the same pyrolysis and aromatization reactions as in the case of thermal conversions of petroleum products. As a result, an entire gamut of aromatic hydrocarbons are produced—benzene, toluene, the xylenes, tri- and tetramethylbenzenes, naphthalene, anthracene, phenanthrene, their homologues and even more complex polycyclic hydrocarbons. The high coking temperature accounts for the nearly complete aromatization of the liquid products formed: the content of compounds of other classes (mainly olefins) in them does not exceed 3-5 percent.

In accordance with the effect of temperature considered above, the coke-oven gas is enriched thermodynamically with more stable hydrocarbons and hydrogen. It contains about 60 percent hydrogen, 15 percent methane, and 2-3 percent ethylene. As an organic raw material, it is of little interest, though from it there is derived not infrequently ethylene, which is used for various syntheses. The coke-oven gas is mainly used as gaseous fuel and for the production of hydrogen.

Coke Ovens. The coal coking process is accomplished in chamber furnaces heated through the wall by flue gases. In order to heat the charge more uniformly, the chambers are made sufficiently narrow

(400-450 mm) and several scores of such vertical chambers are arranged parallel to one another. Thus is built a coke-oven battery with the coke chambers and heating flues alternating from one end to the other. In order to increase the economics of coke ovens it is very important that the heat of flue gases be used as completely as possible. It is for this reason that special regenerators are provided in the furnaces located directly under the chambers. In these regenerators

the hot flue gas heats the packing of refractory brickwork whose heat is then given off to the air and the fuel gas used for combustion.

A by-product coke oven is schematically shown in Fig. 1.16. The furnace has a number of parallel coking chambers 3 which are 4.3 m high and about 14 m long. The vertical flues 4 are interconnected by crossover mains 1. Each heating flue is provided with two regenerators 5 (one for air and the other for fuel gas). The air and fuel gas heated by the hot packing are burned in the lower part of the flue and the gases formed move upwards and enter the next flue through

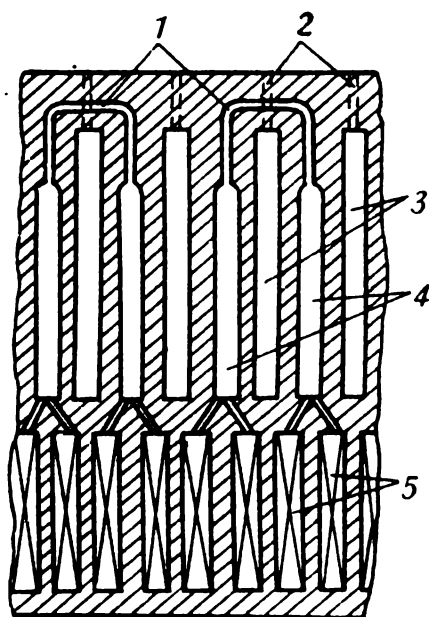


Fig. 1.16. Coke oven.

1—crossover main; 2—standpipes; 3—coke chambers; 4—flues; 5—regenerators.

the crossover main, moving downwards. In the regenerators the gases heat the packing and are removed from the coke oven through a common collecting main. After the first pair of regenerators are cooled the gas stream is reversed, etc. The volatile products are withdrawn from the coke ovens through standpipes 2. The coal blend is charged from the top by means of special larry cars and the red hot coke is pushed out from the furnace by a pusher machine into a quenching car.

Condensation and Recovery of Volatile By-Products. The gas from the oven contains the vapours of organic compounds, water, ammonia, etc. Further processing of the gas consists of the condensation of low-volatile compounds and the recovery of ammonia, pyridine and uncondensed substances.

The volatile materials (*the direct coke oven gas*) leave the oven (Fig. 1.17) through a standpipe and are conducted into a collecting main 2. There the gas is cooled and condensed by contact with a spray of aqueous ammonia liquor known as "flushing liquor". The by-products are cooled here down to 85-90 °C and part of them is condensed. The coke oven gas is then cooled to 30-35 °C in cooler 3,

where an additional amount of tar is condensed. Any tar fog remaining in the gas leaving the cooler is removed by an electrostatic precipitator 4, after which the gas is transferred further by a gas blower 5.

The condensate from collecting main 2, cooler 3 and precipitator 4 separated in decanter 6 into an organic and an aqueous layer. The former is coal tar, which contains higher-boiling organic compounds and is run to the tar-distilling plant for processing. The aqueous layer (ammonia liquor) is partly recycled to the collecting main for primary cooling of the by-products, the remainder being

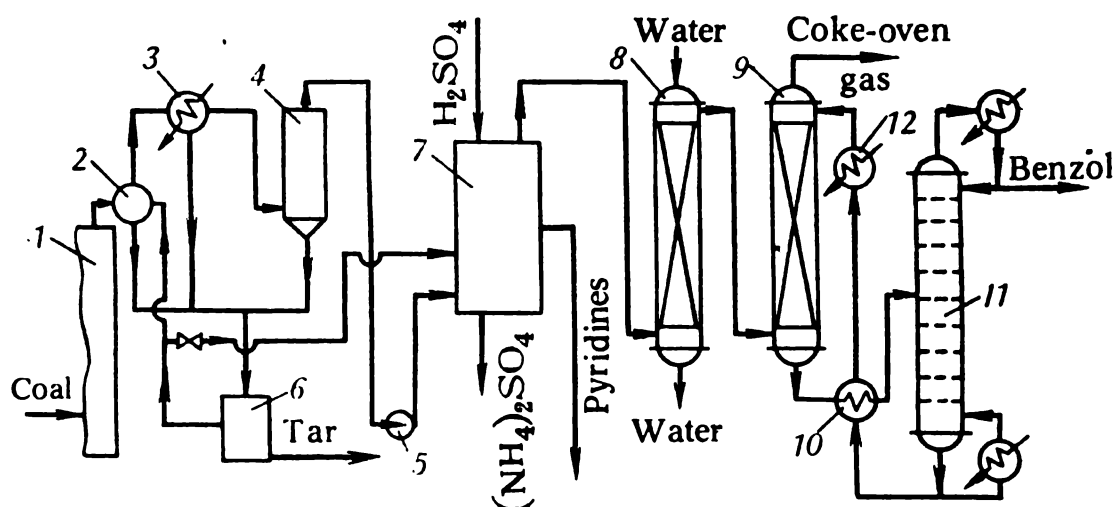


Fig. 1.17. Flow diagram of the condensation and recovery of the volatile products of coal coking:

1—coke oven; 2—gas-collecting pipe; 3, 8, 12—coolers; 4—electric filter; 5—gas blower; 6—separator; 7—unit for recovery of ammonia and pyridine bases; 9—absorber; 10—heat exchanger; 11—desorber.

transferred to unit 7 where ammonia and pyridines are recovered; the gas from the precipitator is also passed to unit 7. This unit has a vaporizer for recovery of ammonia from the flushing liquor, a saturator where nitrogen bases are absorbed by sulphuric acid, a crystallizer for ammonium sulphate and an apparatus for removal of pyridines from their sulphates by ammonia.

The gas from unit 7 still contains vapours of volatile organic compounds (benzene, toluene). For these compounds to be recovered, the gas is cooled by water in direct-mixing cooler 8 and transferred to absorber 9, which is refluxed by an absorbent oil. The *recycle coke-oven gas*, which leaves the absorber, is used to heat the coke ovens, its excess being consumed for other purposes. The saturated absorbent oil from the bottom of the absorber passes through heat exchanger 10, where it is heated by the recycled regenerated oil, and is led to desorber 11. Here fractional distillation takes place, as a result of which a mixture of light aromatic compounds (*crude benzene or benzol*) is distilled off. The absorbent oil freed from the benzol gives up its heat to the saturated oil in heat exchanger 10,

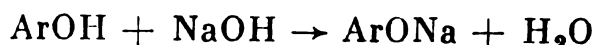
being additionally cooled in cooler 12 and used for the absorption of benzene hydrocarbons from the coke oven gas.

The aromatic hydrocarbons formed upon coking are present in coal tar and benzol. Their composition and processing designed to derive individual compounds will be considered at a later time. The yield of coal tar is 32-34 kg and that of benzol is 10-11 kg per 1 ton of dry coal.

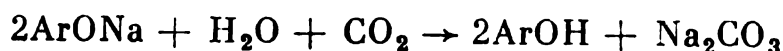
1.3.3. Derivation and Concentration of Aromatic Hydrocarbons

The content of aromatic compounds in the liquid products obtained in various aromatization processes ranges from 30-60 percent (the reforming catalysate) to 95-97 percent (benzol and coal coking tar). Of other hydrocarbons they contain olefins (from 2-3 to 15 percent), paraffins and naphthenes. Apart from these, the coking by-products contain some oxygen-containing compounds (phenol, coumarone), pyridines and also heterocyclic sulphur compounds (thiophene, thiotolene, thionaphthene), which have boiling points close to those of the corresponding aromatic hydrocarbons.

Derivation and Purification of Aromatic Compounds. These processes are carried out on the wide or narrower fractions produced by fractional distillation of the by-products. In the case of benzol and coal coking tar, one of the steps is the derivation of phenols by treatment of the fractions with an aqueous caustic solution:

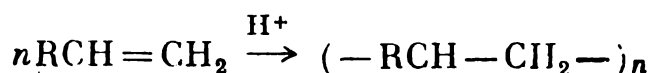
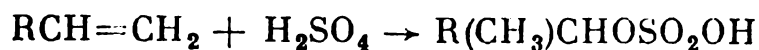


The free phenols are recovered from the caustic solution using carbon dioxide:



This coke-chemical method was the first to be used for the production of phenol, cresols and xlenols.

An important stage is the purification of aromatic fractions from olefins. For coal chemicals containing only a small amount of olefins, use is made of the sulphuric-acid technique, which consists of the treatment of the fractions with 90- to 93-percent H_2SO_4 . In this operation, a portion of olefins gives acidic alkyl sulphates and is transferred to the acid layer, the remainder being polymerized:



The liquid pyrolysis products contain a large amount of olefins and the purification of these products with sulphuric acid is not profitable. To this end, hydrogenation is effected over catalysts that leave the aromatic bonds intact.

For fractions derived from coal tar, the sulphuric-acid purification of olefins is followed by the final fractional distillation for the production of commercial products. However, the fractions of the pyrolysis and reforming products still contain considerable amounts of paraffins, which cannot be separated by ordinary fractional distillation. This is accomplished by the extraction of aromatic hydrocarbons using sufficiently selective solvents (di-, tri- and tetraethylene glycols, dimethylsulphoxide); the selectivity can be increased by adding 5-8 percent of water.

The flow diagram of the derivation of aromatics by extraction is given in Fig. 1.18. The feed hydrocarbon fraction is led to the bottom

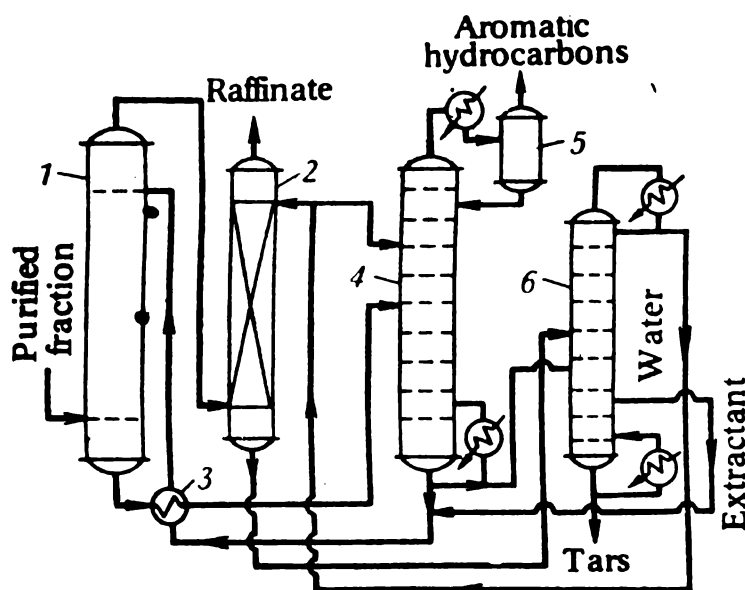
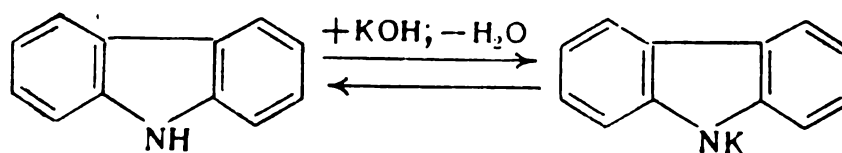


Fig. 1.18. Flow diagram of the extractive separation of aromatic hydrocarbons: 1—extraction column; 2—scrubber; 3—heat exchanger; 4—extractive distillation column; 5—separator; 6—extractant recovery column.

of extraction column 1, where it moves upwards in countercurrent to the extractant introduced at the top of the column. The section between the stream inlets plays the role of a separator. The raffinate from the top of the column entrains some of the extractant which is then recovered by washing the raffinate with water in scrubber 2, following which the raffinate is used as fuel. The saturated extractant from the bottom of column 1 is heated in heat exchanger 3 by the hot regenerated extractant and is passed to column 4, where the extractive distillation of aromatic hydrocarbons with water is effected. In separator 5 the water is separated and returned to column 4 and the mixture of aromatic hydrocarbons is passed to final fractionation. The extractant from the bottom of column 4 is returned, after being cooled, to extraction, a portion of the extractant being withdrawn for regeneration to column 6, where it is freed from excess water and purified from the condensation products. The degree of extraction of aromatic hydrocarbons by this method reaches 93-99 percent.

Aromatic hydrocarbons with condensed rings (naphthalene, an-

thracene, phenanthrene) are largely derived by crystallization methods. The anthracene fractions of coal tar (270-350 °C) are fused with potassium hydroxide and then subjected to hydrolysis to produce another compound, carbazole, which is a valuable raw material for organic synthesis:



Characterization of Fractions of Aromatic Hydrocarbons. There are two major sources for the production of aromatics: coal and petroleum, which differ mainly by the content of organic sulphur compounds. The petrochemical products contain only 0.0001-0.002 percent of sulphur because of the absence of sulphur in petroleum fractions or as a result of hydrotreating, while the content of sulphur in coal chemicals is about 100 times higher. This is of great importance in catalytic methods of processing of aromatic compounds, in which sulphur compounds cause rapid poisoning of catalysts or lead to their increased consumption. The other impurities present are olefins (the bromine number is up to 0.6 g of Br₂ per 100 g) and paraffins (the sulphonation number is not less than 99 percent).

Benzene and *toluene* contain from 99 to 99.9 percent of basic substance, depending on the feedstock.

The *xylene* fractions may differ in the ratio of xylene isomers and in the content of ethylbenzene, which is close in boiling point (136.2 °C) to the xylenes and which is also formed upon thermal decomposition of fuels. The approximate composition of the xylene fractions is as follows (in percent by weight):

	Coal	Petroleum
<i>o</i> -Xylene	10-12	20-24
<i>m</i> -Xylene	52-60	40-45
<i>p</i> -Xylene	14-20	18-20
Ethylbenzene	8-12	14-16

The method of separation of these fractions consists of fractional distillation which is usually combined with the isomerization of the xylenes and the separation of the most valuable *p*-xylene by crystallization or other methods. The crystallization technique will be described below.

Trimethylbenzene is present in the heavy fraction of crude benzene and in 160-180 °C fractions of reforming catalysates and pyrolysis products. Apart from the three isomeric trimethylbenzenes (including pseudocumene, up to 30 percent) the fraction also contains close-boiling isomers of ethyltoluenes and other impurities. Because of

is, the derivation of individual compounds from the fraction is difficult and has been carried out in industry on a small scale.

Tetramethylbenzenes are contained in the 180-210 °C fraction of cracking, pyrolysis and reforming products. The composition of this fraction is even more complex than in the preceding case, and its separation is seldom accomplished on an industrial scale.

Naphthalene is still largely produced from the naphthalene fraction of coal tar (210-230 °C). It is crystallized in water-cooled drum crystallizers, the naphthalene being removed from the drums with a special knife. The crude product is squeezed from the oils upon pressing on hydraulic presses to give pressed naphthalene (the crystallization temperature is not lower than 78 °C and the content of naphthalene is 96-98 percent). The treatment with sulphuric acid and distillation give purer crystalline naphthalene (the crystallization temperature is 79.6-79.8 °C and the naphthalene content is 99-99.5 percent). Sublimated naphthalene isolated as flakes upon sublimation of pressed naphthalene has also assumed some importance.

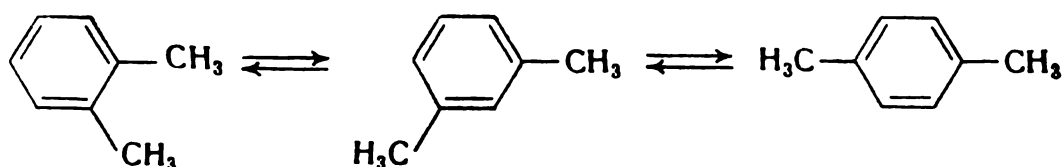
3.4. Production of Aromatic Hydrocarbons

Isomerization and Dealkylation

3.4.1. Isomerization of Aromatic Hydrocarbons

The xylene fractions derived from the products obtained by processing of coal or petroleum contain relatively little *p*- and *o*-xylenes, which are the most valuable isomers. Therefore, methods of isomerization of benzene homologues have been devised and found industrial application for additional production of these hydrocarbons.

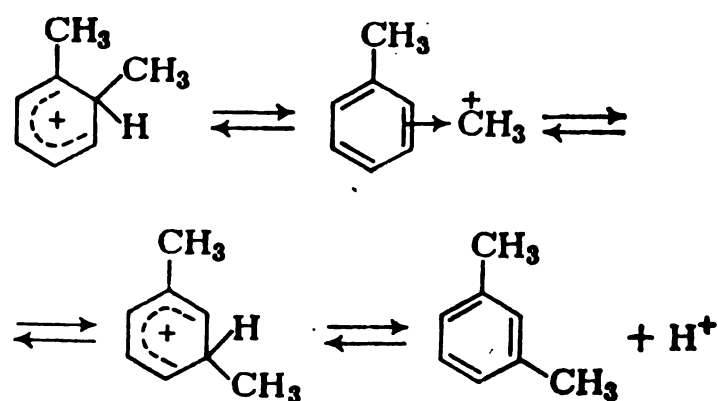
The isomerization of benzene homologues is a reversible process, the equilibrium being established for the xylenes between the three isomers:



At moderate temperature (25-75 °C) the equilibrium mixture contains about 60 percent *m*-xylenes, 24 percent *p*-xylene and 16 percent *o*-xylene, and at 400-500 °C about 52 percent *m*-xylene, 23 percent *o*-xylene and 25 percent *p*-xylene are present. The high content of *o*-xylene is an indication of its high thermodynamic stability.

The isomerization process occurs under the influence of acid-type catalysts. The most active amongst these is aluminium chloride,

which is capable of inducing the reaction in the liquid phase even at 50 °C. In the presence of a heterogeneous silica-alumina catalyst a higher temperature (400-500 °C) is required and the process is carried out in the gas phase. Zeolite (molecular-sieve) catalysts have also found application in recent years. In any case, the reaction proceeds through the intermediate formation of σ -complexes formed from an aromatic compound and of a proton generated by the catalyst. The subsequent process consists of the formation of a π -complex and of the migration of the methyl group to the adjacent carbon atom with subsequent donation of the proton:



In the course of the isomerization of alkylaromatic hydrocarbons there is always present a small amount of by-products, which are substituted benzenes of a lesser or greater degree of alkylation than

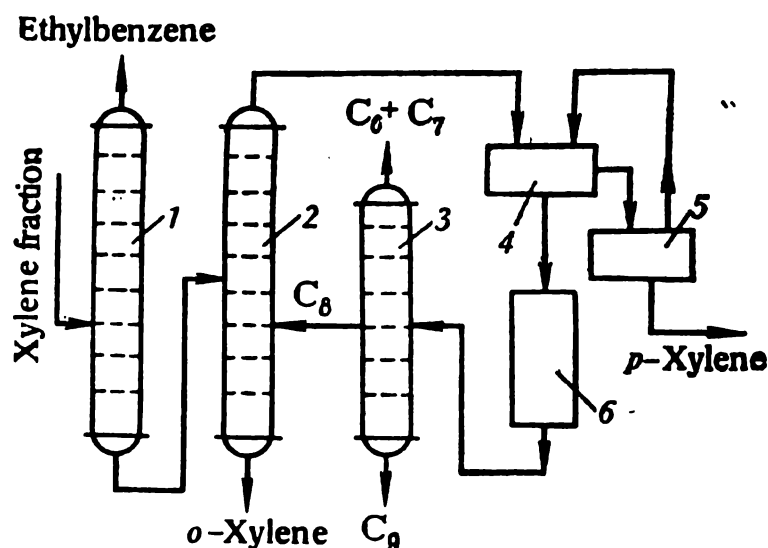


Fig. 1.19. Flow diagram of the separation of the xylene fraction combined with isomerization:

1—ethylbenzene distillation column; 2—o-xylene separation column; 3—column for separation of light and heavy fractions; 4—first-stage crystallization unit; 5—second-stage crystallization unit; 6— isomerization unit.

the feedstock. For instance, the processing of the xylenes gives about 3 percent of the lower homologues (benzene and toluene) and 2-3 percent of polymethylbenzenes.

In industrial practice, the isomerization of the xylenes is always combined with the separation of the corresponding fractions. The flow diagram of the combined processing of the xylene fraction is given in Fig. 1.19.

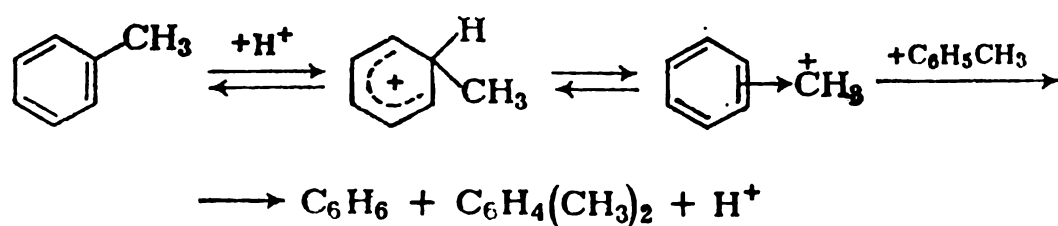
In the first fractionating column 1, from the feed xylene fraction the more volatile ethylbenzene is distilled off. In the second column 2 the combined fractionation of fresh and isomerized xylenes takes place. In the still of this column there is collected the least volatile *p*-xylene, which is removed from the system as the end product. The mixture of *m*- and *p*-xylenes which emerges from the top of column 2 is led to unit 4 of the first crystallization stage, where the mixture is cooled down to -50 to -70 °C. The precipitated crystals are separated by centrifugation. The mother liquor obtained upon filtration contains 75-85 percent of *m*-xylene. It is passed to unit 6 for isomerization; this involves the formation of an additional amount of *o*- and *p*-xylenes. From the isomerized product the by-products (benzene, toluene and polymethylbenzenes) are first separated in column 3 by fractional distillation, the xylenes being passed to column 2. Thus, the major proportion of the product is circulated at the 2-4-6-2 stages.

The solid product obtained as a result of the first crystallization stage contains only 70-80 percent of *p*-xylene. It is melted and subjected to recrystallization in unit 5; after centrifugation 98-percent *p*-xylene is separated. After the second crystallization stage the mother solution contains a considerable amount of the *p*-isomer, which is passed to the first stage of crystallization.

In the processing of the xylene fraction designed to produce only one isomer, say *p*-xylene, there is no need for the second fractionating column, the other stages of the process being the same. There can thus be produced 70 percent of *p*-xylene (based on the feed xylene fraction).

Apart from crystallization, the Parex process of adsorption by zeolites (molecular sieves) described earlier for *n*-paraffins is employed for the derivation of *p*-xylene.

Another process similar to isomerization involves the disproportionation of methylbenzenes using the same catalysts but under more severe conditions. It has found application for the conversion of excess toluene to benzene and the xylenes; the reaction also proceeds via a σ -complex and is accompanied by the intermolecular migration of the methyl group:

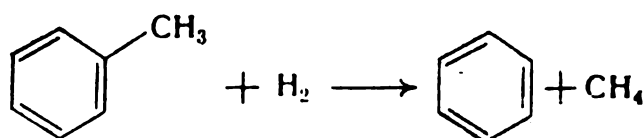


This process is carried out in the gas phase over an aluminosilicate or zeolite catalyst at 350-530 °C and 1-1.2 MPa in the presence of hydrogen, which precludes the coking and lengthens the useful life of the catalyst.

1.3.4.2. Dealkylation of Benzene and Naphthalene Homologues

The large-scale consumption of benzene and naphthalene together with the availability of excess amounts of toluene and methylnaphthalenes accounts for the great practical importance of the processes of dealkylation (demethylation) of aromatic hydrocarbons. Today, considerable amounts of benzene and naphthalene are produced in this way.

The dealkylation of aromatic hydrocarbons is based on their destructive hydrogenation (hydrogenolysis) with the rupture of the carbon-carbon bond between the aromatic ring and the alkyl group:



This reaction can be effected without catalysts (thermal dealkylation) or with heterogeneous catalysts (catalytic dealkylation).

The thermal dealkylation of toluene proceeds well at 700-760 °C. In order to avoid excessive formation of coke and a reduction in the yield of the end products, the process has to be accomplished at 4-5 MPa in the presence of excess hydrogen (4 : 1) with respect to toluene. Under these conditions, it is possible to preclude the dehydrocondensation of aromatic hydrocarbons, this reaction being the cause of coke formation. The nearly 50-percent conversion of toluene with subsequent recycling of the unreacted feedstock with the yield of benzene reaching 98 percent of theoretical has been reported.

The catalytic dealkylation of aromatics is carried out with such dehydro-hydrogenating catalysts which are active with respect to the destructive hydrogenation and which do not affect the aromatic ring. Such catalysts include molybdenum, cobalt and chromium oxides, of which chromium oxide on an active aluminium oxide support has found practical application. In order to avoid coke deposition on the catalyst surface and its rapid deactivation, the process is effected at a hydrogen pressure of 3-10 MPa. Just as in the case of thermal dealkylation and catalytic reforming, hydrogen prevents dehydrocondensation reactions. The temperature used for catalytic dealkylation is only slightly lower than in thermal dealkylation and is 580-620 °C. The yield of benzene from toluene may exceed 95 percent of theory.

1.3.4.3. Estimation of Method of Producing Aromatic Hydrocarbons

The yields of aromatic hydrocarbons obtained in coking, pyrolysis and reforming processes are as follows (in kg per 1 ton of coal or crude oil):

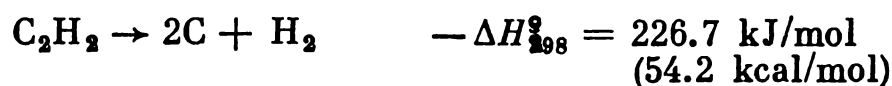
	Coal coking	Pyrolysis of lignin	Platforming of lignin
Benzene	6-6.5	7-9	5-10
Toluene	1.5	4-6	5-7
Xylenes	0.3	1.5-2.5	1-3
Naphthalene . . .	2-2.5	2-3	—

The yield of petroleum-based aromatics from the corresponding oil fractions is about 10 times higher than the figure indicated above.

In estimating the role of each of the processes used, one should keep in mind that in coking and pyrolysis processes aromatic hydrocarbons are obtained as by-products in the production of coke and olefins and that their utilization improves the economics of production. Therefore, up to now about 10 percent of benzene hydrocarbons and all naphthalene are produced by the coal carbonization process. In Western Europe, pyrolysis has assumed preponderant significance for the production of aromatics, and its position in the world has been strengthened in connection with the switch to the liquid raw material, which provides an increased yield of aromatics and butadiene. The excess toluene produced is profitably processed to benzene and xylenes (for instance, in the United States, in 1976, 30 percent of the total amount of benzene was produced by the hydrodealkylation of toluene). Finally, it is expedient to manufacture the missing amount of benzene and xylenes by a process designed for the production of aromatics—the reforming of narrow petroleum fractions.

1.4. Acetylene

Acetylene is a colourless gas which has a weak etherial odour in the pure state; it is condensed at -83.8°C (0.098 MPa); the critical temperature is $+35.5^{\circ}\text{C}$; the critical pressure is 6.04 MPa. Acetylene is highly inflammable and forms explosive mixtures with air (2.0-81 percent by volume of C_2H_2) and oxygen (2.8-78 percent by volume of C_2H_2). The high inflammability of acetylene is aggravated by the high exothermicity of its decomposition into its elements:



The decomposition of acetylene proceeds in the absence of oxygen and the presence of appropriate initiators (a spark, overheating due

to friction). At a pressure of up to 0.2 MPa the decomposition is local and is not dangerous. At a higher pressure the decomposition becomes explosive, the detonation wave spreading with a velocity greater than 1000 m/s. The explosiveness of acetylene is lowered when it is diluted with inert gases or vapours, which accumulate the heat of the primary decomposition of acetylene and which prevent its explosive decomposition. In such cases the maximum safe pressure of the mixture depends on the acetylene concentration (Fig. 1.20).

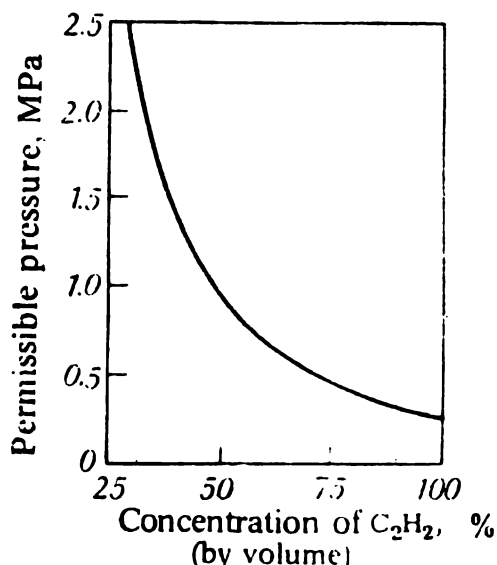


Fig. 1.20. Dependence of the permissible maximum pressure on the concentration of acetylene in its mixtures with nitrogen.

The inflammability of acetylene greatly increases in the presence of metals capable of forming acetylides (say, Cu_2C_2), a fact that must be kept in mind in choosing materials of construction.

In order to avoid explosions, the most common practice is to limit the pressure in the production of acetylene and in various syntheses to 0.2 MPa. If the operations are to be carried out under pressure, acetylene is diluted with nitrogen and sometimes with vapours of reactants. When acetylene is compressed, use is made of special acetylene compressors with a low velocity of the

movable parts, a low compression ratio and a temperature after each stage of the compressor not exceeding 100 °C. The apparatus and pipelines are designed with an increased safety factor. Besides, special safety devices are employed, which are located at various points in the system. Dry-type shut-off devices (in the form of ball valves) prevent only the propagation of the flame. Wet-type fire interrupters and hydraulic gates prevent the flame from striking back into the preceding apparatus. The fire interrupter is a tower filled with a packing sprayed with water and the hydraulic gate is a device in which acetylene bubbles through a water layer. In all cases, when the pressure limit is exceeded, the gases are discharged into the atmosphere through the hydraulic gates or protective diaphragms.

Another technically important property of acetylene is its solubility, which is much higher than the solubility of other hydrocarbon gases. For example, at 20 °C about 1 volume of acetylene is dissolved in 1 volume of water, and at 60 °C 0.37 volume is dissolved. The solubility of acetylene decreases in aqueous solutions of salts and $\text{Ca}(\text{OH})_2$. The solubility of acetylene is considerably greater in organic liquids; at 20 °C and atmospheric pressure it is as follows (in

acetylene volumes per one volume of solvent): 11.2 in methanol, 23 in acetone, 32 in dimethylformamide, 37 in N-methylpyrrolidone. The solubility of acetylene is of great importance in its production and separation from mixtures with other gases and also in acetylene cylinders, in which a solvent (acetone) is used in order to increase their capacity for acetylene and to reduce its pressure.

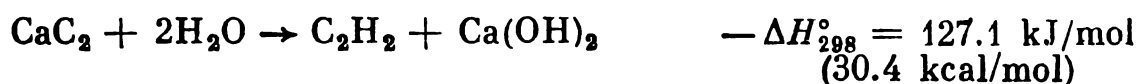
There are two methods of acetylene production: the older method from calcium carbide and the new one, from hydrocarbons.

1.4.1. Production of Acetylene from Calcium Carbide

As known, calcium carbide is produced from calcium oxide and coke in electric arc furnaces:



The reaction is strongly endothermic and requires the consumption of large quantities of electric power, which constitutes an essential factor in the cost of acetylene production. The decomposition of the calcium carbide formed with water by an exothermic reaction leads to acetylene:



From 1 kg of technical-grade calcium carbide, which contains impurities of coke, calcium oxide and other substances there is produced 230-280 litres of acetylene (this is called the *carbide capacity*). Theoretically, from 1 kg of pure CaC_2 there must be obtained 380 litres of C_2H_2 .

During the decomposition of calcium carbide certain conditions must be observed to provide the normal development of the process. The reaction is heterogeneous and its velocity depends on the size of carbide lumps, increasing especially strongly when carbide fines or dusts are used. The reaction mass must be stirred, since otherwise a layer of lime may be formed on carbide lumps which hinders the complete decomposition of the carbide and causes local overheating. It is necessary to constantly remove the heat from the reaction zone in order to prevent the polymerization and decomposition of acetylene.

Acetylene Generators. The units in which the decomposition of calcium carbide with water is carried out are called *acetylene generators*. According to the manner of heat removal, these generators are of two types:

1. Wet-type generators in which the reaction heat is taken up by the excess water, which is thus heated to 50-60 °C. About 10 kg of

water is consumed per 1 kg of CaC_2 , the calcium hydroxide being obtained in the form of a suspension in water which is unsuitable for subsequent utilization.

2. Dry-type generators in which the reaction heat is removed by a small amount of excess water due to its evaporation. In this case, calcium hydroxide is produced in the dry state (the air-slaked lime) and it can be easily used for the manufacture of construction materials.

Wet-type generators are divided into the following systems according to the manner in which the reactants are charged: the carbide-into-water type, the water-on-carbide type and the contact type, in which the water and carbide are in constant contact. Carbide-into-water generators are the safest and most suitable for the large-scale manufacture of acetylene. In these units, carbide lumps are immersed into excess water, which precludes overheating and provides conditions for the better removal of the reaction heat.

The diagram of a typical carbide-into-water generator is given in Fig. 1.21. The apparatus is nearly $3/4$ filled with a water suspension of calcium hydroxide. The calcium carbide in the form of lumps 50-80 mm in size is fed to intermediate hopper 1, into which nitrogen is introduced to

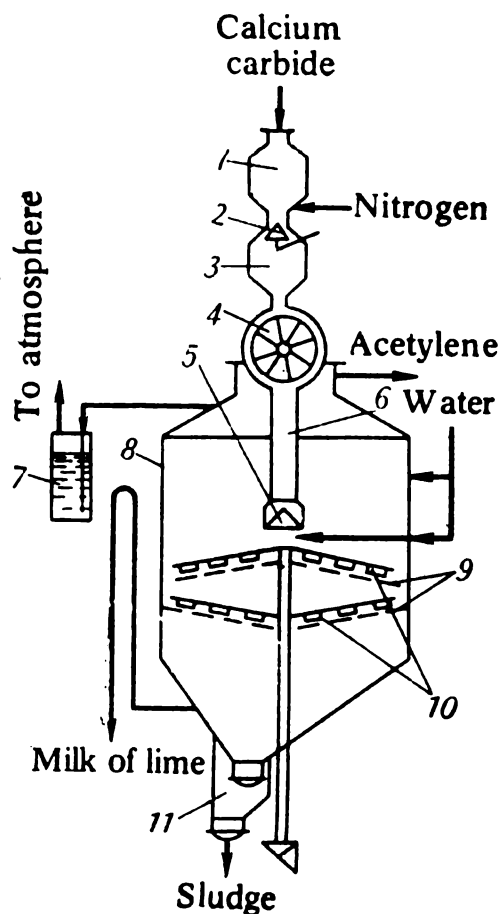


Fig. 1.21. Schematic of the acetylene generator of the "carbide-into-water" system:

1, 3—hoppers for carbides; 2—conical plug; 4—sector drum; 5—distributor cone; 6—feed pipe; 7—hydraulic seal; 8—body; 9—perforator trays; 10—scraper mixer; 11—gate valve.

displace the air. Then, the conical plug 2 is opened and the carbide is discharged into feeding hopper 3. The supply of the carbide is automatically proportioned by sector drum 4; the speed of its rotation is controlled, depending on the demand for acetylene. The carbide lumps are led through pipe 6, whose end is immersed in a liquid, onto cone 5 and are uniformly distributed along the cross section of the generator. The decomposition of the carbide occurs on inclined perforated trays 9, the pieces being moved from the centre of the shelves to the periphery and back by scraper mixer 10. The layer of lime sludge is removed from the carbide pieces by means of the mixer.

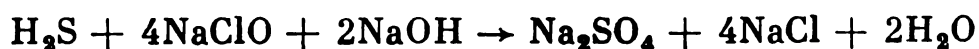
The decomposition of the carbide by water gives a solution-suspension of calcium hydroxide in water (milk of lime) and a sludge consisting of solid inert impurities present in the carbide feedstock (coke, ferrosilicon). The sludge settles at the bottom of the generator and is collected in gate valve 11, from which it is periodically discharged. The milk of lime is removed continuously from the bottom of the generator and allowed to settle down. The clarified solution with fresh water added to it is returned to the generator to decompose the carbide, which precludes considerable losses of acetylene caused by its dissolution in water. The water supply is regulated automatically, depending on the demand for acetylene. The acetylene formed is withdrawn from the generator, and if the pressure in the apparatus increases and exceeds the permissible level (400-450 MPa), the excess gas is exhausted into the atmosphere through hydraulic gate 7. The capacity of carbide-into-water generators amounts to 500 m³ of acetylene per hour.

The capacity of dry generators in which the carbide fines are processed is even higher. The main condition for their successful operation is the close contact between the carbide particles and a small amount of water. This is achieved by introducing water through special sprayers and by using mixers in the generator (revolving drums, scraper mixers). This precludes overheating of acetylene and maintains a uniform temperature of 110-115 °C.

Impurities and Purification of Carbide Acetylene. When leaving the generator the acetylene has a high concentration (above 99 percent by volume), but contains small amounts of impurities of NH₃, H₂S, PH₃, etc. These are formed upon decomposition by water of compounds that are always present in calcium carbide, in particular the nitrides, sulphides and phosphides of calcium and other metals:



These compounds are found to be very harmful in the chemical processing of acetylene, since they are capable of deactivating or poisoning the catalysts (for example, they reduce mercuric salts) and purification is a requisite stage in the manufacture of carbide acetylene. For this purpose, use is most often made of aqueous solutions of sodium hypochlorite which oxidize the impurities to the corresponding acids; an example is the following reaction:



The flow diagram of acetylene production from calcium carbide in a wet-type generator is shown in Fig. 1.22. Calcium carbide is transported in larry cars 1 which run on monorails 2 and is poured into the hopper of the wet-type generator 6. The milk of lime obtained

in the generator upon decomposition of the carbide is led to continuous-action settler 5 equipped with a scraper mixer, which moves the settled slurry to the central drain nozzle. The lime slurry is then pumped by means of a special pump into settling pits. The clarified calcium hydroxide in water is returned from settler 5 through cooler 4 into pressure tank 3, where a certain amount of fresh water is added to it to compensate for its loss. From the pressure tank the water is passed to generator 6.

The acetylene formed in the generator has a temperature of 50-60 °C; it is cooled in cooler 7, separated from the condensate and passed

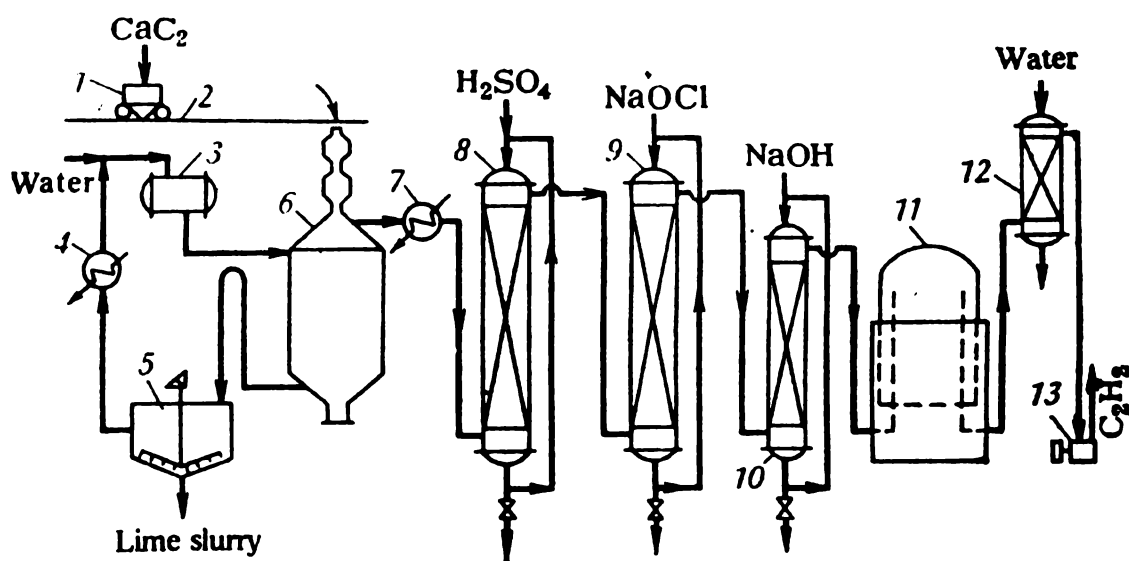


Fig. 1.22. Production of acetylene from calcium carbide:

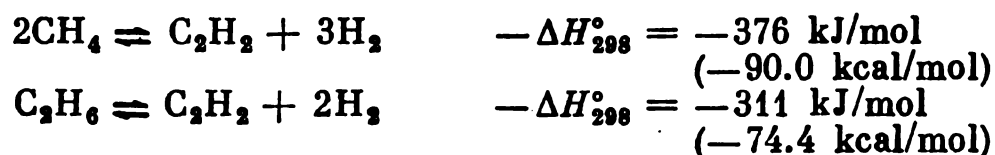
1—larry car; 2—monorail; 3—pressure tank; 4, 7—coolers; 5—decanter; 6—acetylene generator; 8, 9, 10—scrubbers for purification of acetylene; 11—wet gas holder; 12—fire interrupter; 13—compressor.

through packed scrubber 8 refluxed by a solution of sulphuric acid. In this scrubber the acetylene is freed from the ammonia residues, part of which has been dissolved in the water from the generators and in the condensate from cooler 7. The gas is then led to scrubber 9 refluxed by a water solution of sodium hypochlorite and, finally, to caustic scrubber 10 to be purified from the traces of chlorine entrained in the hypochlorite column. All the absorbent solutions are circulated by centrifugal pumps; a proportion of the spent solution is periodically removed from the system and replaced by a fresh solution. The purified acetylene is collected in "wet" gas holder 11, from which it is transported to the consumer by means of a compressor or gas blower 13 through a protective hydraulic gate or fire interrupter 12.

When acetylene is produced in dry-type generators, there is no need for settler 5 and cooler 4, but the purification step remains the same.

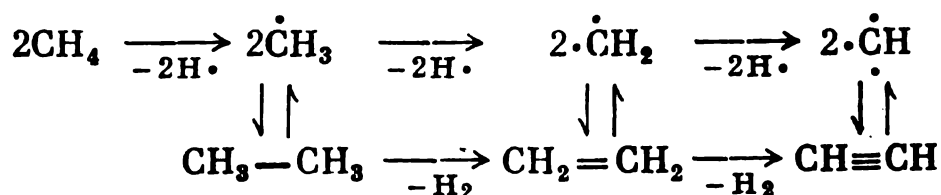
1.4.2. Production of Acetylene from Hydrocarbons

From methane and other paraffins, acetylene is obtained by a high-temperature pyrolysis according to the following reactions:



These reactions are endothermic and their equilibrium is shifted to the right only at 1000-1300 °C (Fig. 1.23). However, in practice the process has to be carried out at higher temperatures in order to speed it up: 1500-1600 °C for methane and 1200 °C for liquid hydrocarbons.

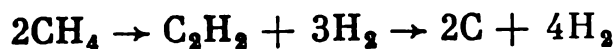
Like the pyrolysis for olefins, the reactions of formation of acetylene proceed by a radical-chain mechanism, the sequence of methane and ethane conversions being approximately as follows:



Apart from the lower paraffins and olefins, the gas produced in these reactions contains also a small amount of benzene and acetylene hydrocarbons—methylacetylene ($\text{CH}_3-\text{C}\equiv\text{CH}$), vinylacetylene ($\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$), diacetylene ($\text{CH}\equiv\text{C}-\text{C}\equiv\text{CH}$), etc.

The production of acetylene by this method is complicated by a side reaction—its decomposition into carbon and hydrogen.

This side reaction becomes appreciable at 1000 °C and attains a considerable velocity at 1200-1600 °C, i.e., at the temperature required for the production of acetylene. As a result, there occurs a series of consecutive reactions, in which the acetylene formed decomposes into hydrogen and carbon black:



Just as in other similar cases, the yield of the intermediate product can be controlled by lowering the degree of conversion of the hydrocarbon feedstock achieved by reducing the contact time. It has been

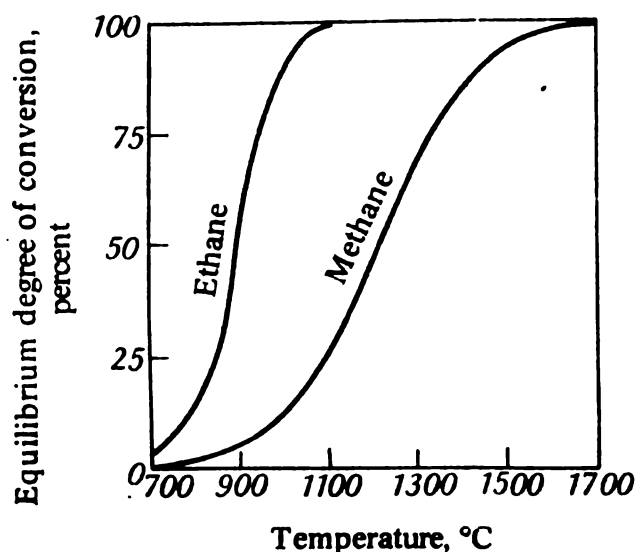


Fig. 1.23. Temperature dependence of the equilibrium degree of conversion of methane and ethane to acetylene at ≈ 0.1 MPa.

found that a good yield of acetylene with the formation of a small amount of carbon black can be obtained if the degree of conversion of the hydrocarbon feedstock is about 50 percent and its residence time in the reaction zone is less than 0.01 s. In order to prevent further decomposition of acetylene, a rapid quench of the reaction gases (injection of water) is required—the temperature falls off sharply to a temperature at which acetylene does not decompose.

Methods of Pyrolysis of Hydrocarbons to Acetylene. According to the manner in which the heat is supplied for conducting the highly endothermic reaction of pyrolysis of hydrocarbons to acetylene, four methods are distinguished:

1. *Regenerative pyrolysis* in furnaces containing refractory brick; the refractory brick is heated by flue gases and then the feedstock to be pyrolyzed is passed through the red hot brick. These runs alternate.

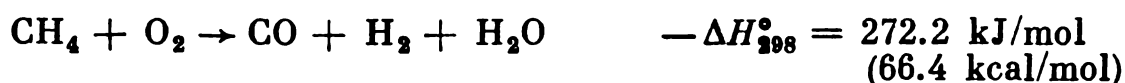
2. *Electric cracking* effected by means of an electric arc, in which case the hydrocarbon feedstock is subjected to pyrolysis in electric-arc furnaces at an interelectrode voltage of about 1000 V. The power consumption can be as high as 13,000 kW·h per 1 ton of acetylene, which is the main shortcoming of the method.

3. *Homogeneous pyrolysis*, in which the feedstock is introduced into the stream of the hot flue gas, which is obtained by burning methane in oxygen and which has a temperature of about 2000 °C. This technique may be combined with other pyrolysis processes if the vapours of liquid hydrocarbons, which can be decomposed to acetylene at a lower temperature, are introduced into the hot off-gas of the first stage of pyrolysis. The additional feature of this process is that ethylene may be obtained as a co-product.

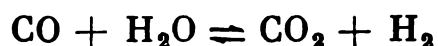
4. *Oxidative pyrolysis* in which the exothermic reaction of combustion of hydrocarbons and endothermic pyrolysis are combined in a single apparatus.

All these methods of pyrolysis of hydrocarbons to acetylene are carried out on an industrial scale, but the most economical of these processes is oxidative pyrolysis. Let us consider it in more detail.

With a deficiency of oxygen and a high temperature the combustion of methane occurs mainly according to the reaction



This reaction proceeds very rapidly and the formation of acetylene (as the slower process) starts only in the zone which is practically free of oxygen. In this zone, the conversion of carbon monoxide also takes place:



the ratio of hydrogen, carbon monoxide, carbon dioxide and steam being close to this water-gas equilibrium (which is known as the

shift reaction at present). In practice, about one-third of oxygen is consumed for the formation of water, 10-15 percent for CO_2 and 50-55 percent for CO.

Since the process is conducted under automatically controlled thermal conditions, for the temperature of about 1500°C required for the decomposition of methane to be maintained, the ratio of the initial volumes of CH_4 and O_2 must be equal to 100 : (60-65), which is outside the explosive limits of these mixtures. Dangerous concentrations may arise only during the mixing operation, which is carried out at a sufficiently high rate and turbulence of the gas stream. The combustion of methane is characterized by a certain induction period, whose duration depends on temperature and pressure. For methane-oxygen mixtures of the above-indicated composition, at atmospheric pressure and 600°C the induction period is about 2 s, which limits the time from the moment of mixing of the preheated gases to their entry into the burners, where the spontaneous ignition of the mixture occurs. The velocity of the gas stream in the burner nozzle (about 100 m/s) must be higher than the velocity of propagation of the flame to prevent the flame from striking back into the mixing section. At the same time, under stable combustion conditions the gas velocity must not be higher than the velocity of flame extinguishing to prevent the detachment of the flame from the burner. With a turbulent flow, stable combustion is favoured by the supply of an additional amount of oxygen into the combustion zone (the so-called stabilizing oxygen) and also by multinozzle devices with numerous flames which are mutually stabilized.

The schematic of one of the reactors widely employed for the oxidative pyrolysis of methane is given in Fig. 1.24. Its body 2 is lined with a very refractory material. Methane and oxygen enter mixing chamber 1, pass through diffuser 8 fitted with a protective diaphragm 3 and are led into the orifices on a burner block 7, the stabilizing oxygen being injected below the block. In chamber 4 the methane is partly burned and acetylene and carbon black are formed. Quench water is injected through sprayers 6 and the pyrolysis products are

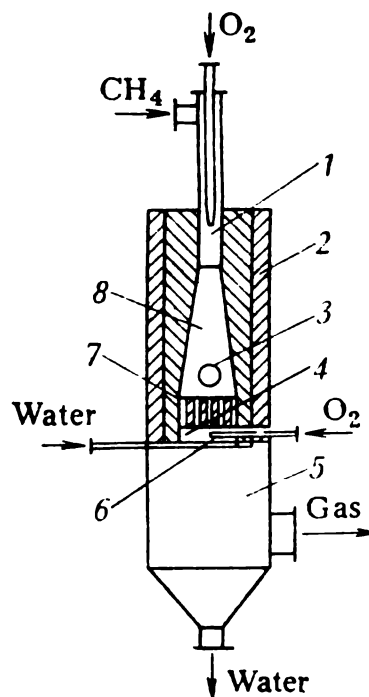


Fig. 1.24. Reactor for the oxidative pyrolysis of methane to acetylene:

1—mixing chamber; 2—body; 3—safety diaphragm; 4—combustion chamber; 5—lower chamber; 6—sprayer; 7—burner block; 8—diffuser.

cooled immediately. The pyrolysis gas is removed from the lower chamber 5, where a proportion of the coke formed settles and is then removed together with the water. Under the normal conditions of oxidative pyrolysis 55 percent of methane is consumed for combustion, 23-25 percent for the formation of acetylene, about 4 percent for the formation of carbon black; the degree of conversion of methane reaches 90 percent and the degree of conversion of oxygen exceeds 99 percent.

The Composition of Pyrolysis Gases and Their Separation. The reaction gases obtained on pyrolysis have a complex composition and contain only 7-9 percent by volume of C_2H_2 (upon oxidative and homogeneous pyrolysis) or 11-14 percent (by volume) of C_2H_2 (in electrocracking and regenerative pyrolysis). The basic components of the gases are H_2 (45-55 percent by volume) and CH_4 (5-25 percent by volume); in the case of oxidative and homogeneous pyrolysis the gases contain CO (26-27 percent by volume) and CO_2 (3-4 percent by volume). The content of acetylene homologues reaches 0.2-0.3 percent (by volume) in oxidative pyrolysis and 1-1.5 percent (by volume) in the other cases.

For the derivation and purification of acetylene, use is made of its property to dissolve better than the other components of the reaction off-gases in certain agents: in methanol or acetone upon cooling down to $-70^\circ C$ and especially in dimethylformamide and N-methylpyrrolidone at room temperature. The common practice is to separate the gas first from the carbon black and then from the more soluble aromatics and acetylene homologues (preabsorption), following which the acetylene is absorbed. The purification is effected by means of stepwise desorption.

The flow diagram of acetylene production by oxidative pyrolysis of methane is given in Fig. 1.25. Oxygen and methane are heated to 600-700 $^\circ C$ in tubular furnaces 1 and 2, which are equipped with burners for the combustion of natural gas. The processes described above take place in reactor 3; the gases emerge from the reactor after water quenching at 80 $^\circ C$ and pass through hollow water scrubber 4 and wet-film electric filter 5 for the carbon black to be separated. The gases are cooled with water in direct-mixing cooler 6, following which they are washed in preabsorber 7 with a small amount of dimethylformamide (DMF) or N-methylpyrrolidone and are led into gas holder 8. The water running from the hydraulic seal of the reactor and from the carbon-black catcher contains 2-3 percent of carbon black and also low-volatile aromatic hydrocarbons. It enters carbon-black settler 9, from the top of which the carbon black and tars are collected by scrapers and passed to burners. The water from the carbon-black settlers is returned to the reactor as a quench agent and its excess is used for purification, this creating a closed circuit water system without discharging toxic waste waters.

The gas from gas holder 8 is compressed by compressor 10 to about 1 MPa and passed after each stage through coolers and separators not shown in the diagram. In absorber 11 the gas is flushed with dimethylformamide or N-methylpyrrolidone and the unabsorbed gas (H_2 ,

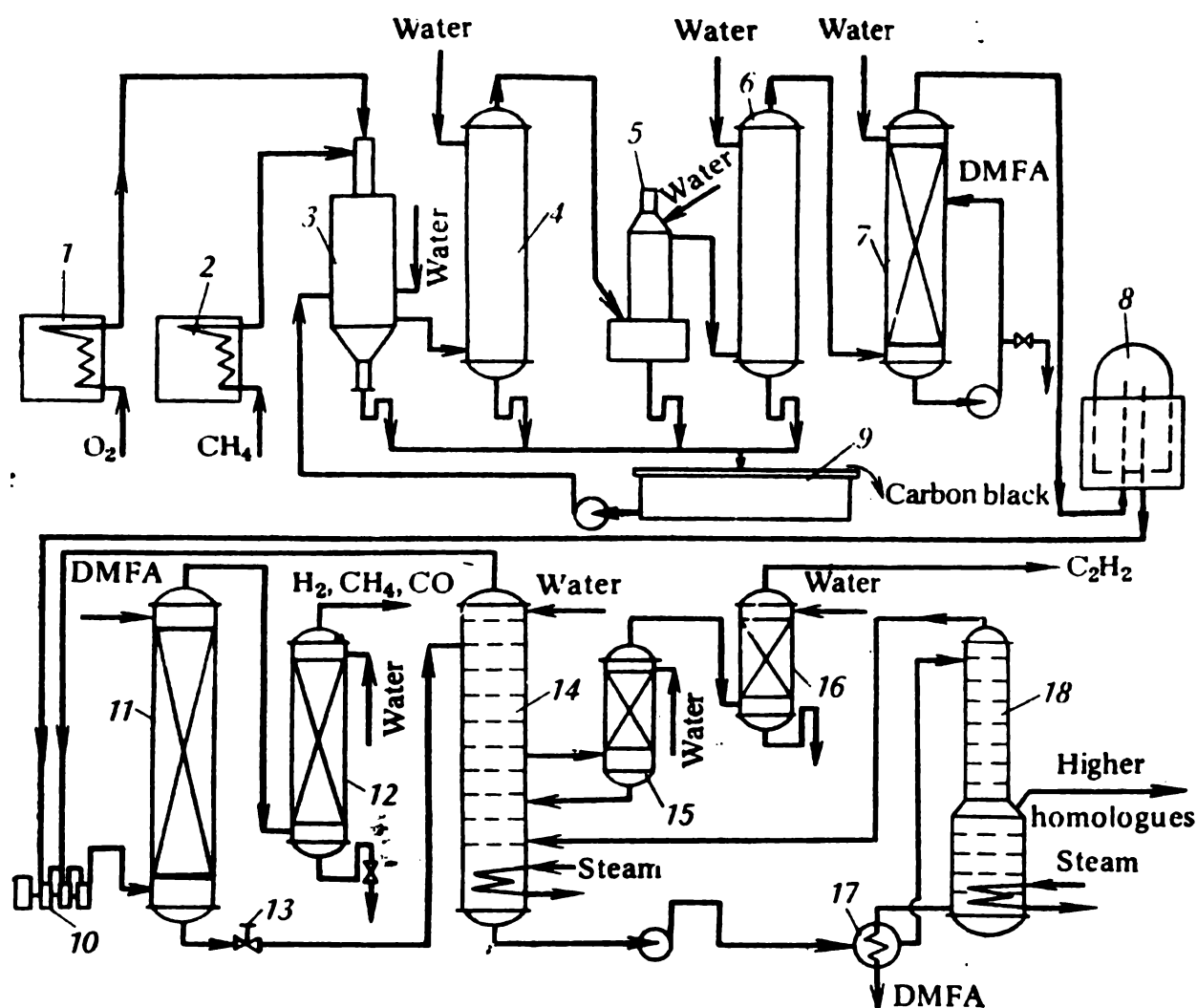


Fig. 1.25. Flowsheet for production of acetylene by oxidative pyrolysis of methane:

1, 2—tubular furnaces; 3—acetylene reactor; 4—scrubber and carbon-black collector; 5—wet-film electric filter; 6—cooler; 7—preabsorber; 8—gas holder; 9—carbon-black precipitator; 10—compressor; 11—absorber; 12, 15—water scrubbers; 13—throttle valve; 14, 18—desorbers; 16—fire interrupter; 17—heat exchanger.

CH_4 , CO , CO_2) passes through scrubber 12, where the solvent entrained by it is recovered by refluxing with the water condensate. After this, the gas can be used as a synthesis gas or fuel.

The solution in the still of absorber 11 contains acetylene and its homologues and also a considerable amount of carbon dioxide, which is almost as soluble as acetylene, and impurities of other gases. The solution passes through throttling valve 13 and enters first-stage desorber 14. As a result of the pressure being lowered to about 0.15 MPa and the still being heated up to $40^\circ C$, the acetylene and the less soluble gases are desorbed from the solution. While moving upwards the acetylene displaces from the solution the carbon dioxide, which together with the other gases and a proportion of acetylene

leaves the top of the desorber after being preliminarily washed off from the solvent by the water condensate. These gases are returned to compression. The concentrated acetylene is withdrawn from the middle section of desorber 14, washed in scrubber 15 with water and removed from the unit through fire interrupter 16.

The still liquid of desorber 14, which contains a certain amount of acetylene and its homologues is led to second-stage desorber 18 after being preheated in heat exchanger 17. All the gases are distilled off from the solution by heating the still up to 100 °C, the acetylene homologues being removed from the middle part of the column and sent for combustion; the acetylene admixed with its homologues is taken overhead and returned to the first-stage desorber. In the solvent there are gradually accumulated water and polymers, which are separated from the solvent in the regeneration unit not shown in the diagram.

The concentrated acetylene obtained in the unit is 99-99.5 percent pure and contains methylacetylene, propadiene and carbon dioxide (up to 0.1-0.3 percent).

1.4.3. Comparison of Methods of Acetylene Production

The main shortcomings of the carbide method of acetylene production are the large consumption of electric power for the manufacture of calcium carbide and the multistage nature of the conversion of the feedstock ($\text{CaCO}_3 \rightarrow \text{CaO} \rightarrow \text{CaC}_2 \rightarrow \text{C}_2\text{H}_2$) and a considerable capital investment. The advantage of the process is the production of concentrated acetylene, whose purification from a small amount of impurities presents no difficulties. Besides, the production of carbide acetylene is based on coal, which is more available.

The production of acetylene by the pyrolysis of hydrocarbons involves one step, requires lower capital investment and less electric power (except for electrocracking). The acetylene is produced diluted, however, and a rather complex separation and purification system is required.

There are numerous conflicting estimates of the economic efficiency of these processes which will undoubtedly be influenced by the problems of the availability of petroleum and natural gas. At the present time, more than half of the world's acetylene production comes from the carbide method.

1.5. Carbon Monoxide and Synthesis Gas

Organic synthesis employs both pure carbon monoxide and its mixtures with hydrogen (synthesis gas) in the volume ratio from 1 : 1 to 2-2.3 : 1. *Carbon monoxide*, CO, is a colourless, difficultly liquefi-

ble gas (b.p. -192°C at atmospheric pressure; the critical pressure 43 MPa; the critical temperature -130°C). With air it forms explosive mixtures over the concentration of 12.5-74 percent by volume. Carbon monoxide is very poisonous and its maximum permissible concentration on industrial premises is 20 mg/m^3 . Ordinary gas masks do not adsorb carbon monoxide and use is therefore made of isolation-type gas masks or gas masks in which a layer of hopcalite is placed in the canister below the adsorbent bed (hopcalite is a mixture of 10% manganese dioxide, 30% copper oxide, 15% cobaltic oxide, and 5% silver oxide and is used to convert carbon monoxide to carbon dioxide by reaction with atmospheric oxygen). Carbon monoxide is slightly sorbed not only by solids but also by liquids, in which it dissolves with difficulty. Some salts, however, form complexes with carbon monoxide, this reaction being used for the sorption of carbon monoxide by ammonio-cuprous salt solutions.

Hydrogen, the second component of the synthesis gas, is the most difficultly liquefiable gas (b.p. -252.8°C at atmospheric pressure). When mixed with air (oxygen) it forms explosive mixtures, the flammability limits being 4.0 to 75% (by volume). Together with the high flammability of carbon monoxide, this imposes increased safety requirements in the production of synthesis gas and also in plants where it is used as a raw material for organic synthesis.

The original production of synthesis gas was based on coal, but subsequently the conversion of hydrocarbons assumed predominant importance; two variants of the process are employed: catalytic and high-temperature conversion. The raw material may be methane or natural gas and also liquid petroleum fractions.

1.5.1. Production of Synthesis Gas by Catalytic Conversion of Hydrocarbons

The basic reaction is the conversion of hydrocarbons by steam over a nickel catalyst supported on Al_2O_3 :



The reaction is strongly endothermic and its equilibrium is shifted to the right only at an elevated temperature (Fig. 1.26, curve 1). In order to increase the degree of conversion of methane, the process is carried out at $800\text{-}900^{\circ}\text{C}$ in an excess of steam. At atmospheric pressure this excess of steam is not large (2 : 1), but an increase in pressure has an unfavourable effect on the state of equilibrium, and in this case the steam-methane volume ratio has to be about 4 : 1.

Apart from the methane conversion, there also takes place the

conversion of carbon monoxide:



This reaction is exothermic and its equilibrium is shifted to the left at an elevated temperature (Fig. 1.26, curve 3); the excess steam causes the formation of a larger amount of carbon dioxide. The conversion of carbon monoxide proceeds rapidly and the composition of the converted gas depends on its equilibrium.

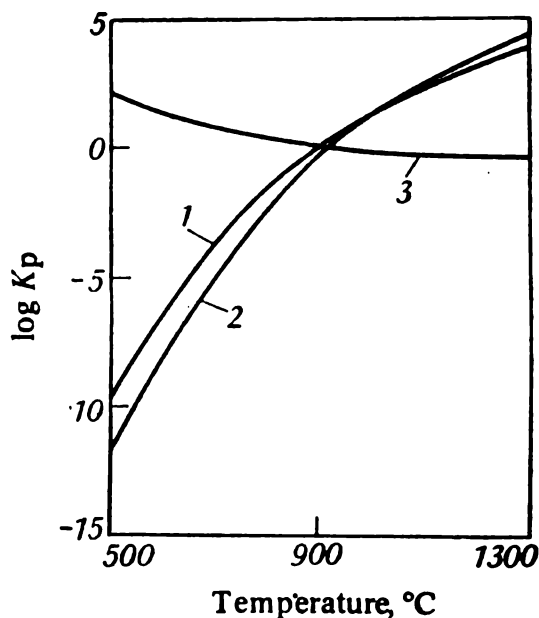
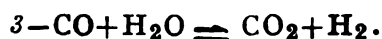
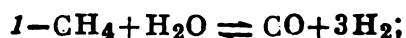


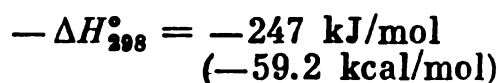
Fig. 1.26. Temperature dependence of the equilibrium constants of the conversion reactions:



The conversion of methane by steam yields a gas with a large hydrogen-carbon monoxide ratio (3 : 1 as a minimum), while for organic synthesis there is required synthesis gas with an H_2/CO ratio of 1 : 1 to (2-2.3) : 1. Such a ratio can be achieved by conversion of liquid hydrocarbons:



or by addition of carbon dioxide to steam during the conversion, the carbon dioxide also converting the hydrocarbons:



The reaction is endothermic and its equilibrium is shifted to the

right at a sufficiently high temperature (Fig. 1.26, curve 2). It proceeds at a slower rate than the methane-steam reaction.

Since the reaction is highly endothermic, the conversion of hydrocarbons is carried out in tubular reactors (Fig. 1.27a). The feedstock is introduced into the tubes filled with a heterogeneous catalyst and heated by a flue gas, the heat transfer being effected mainly due to radiation (radiant furnaces). The shortcomings of this system are the need for heat-resistant tubes and the inefficient use of the reactor, in which the catalyst occupies only a small space.

In view of this, another system was developed, in which the endothermic conversion reactions are combined with the exothermic combustion of a portion of the hydrocarbon when oxygen is supplied into the converter, as a result of which the overall process becomes slightly exothermic. Calculations show that for this purpose the CH_4-O_2 mixture to be converted must be in the ratio of 1 : 0.55, which is outside the explosive limits that cannot be reached because

of the mixture being diluted with steam. The volume ratio of steam to methane may here be lower than in the absence of oxygen, namely from 1 : 1 to (2.5-3) : 1, depending on the pressure used. This *process of oxidative or autothermal conversion* has found wide application. It does not require an external heat supply system and is effected in shaft furnaces with a continuous catalyst bed (Fig. 1.27b).

The converter is lined with refractory brick and has a cooling water jacket, in which steam is generated. In the top of the converter

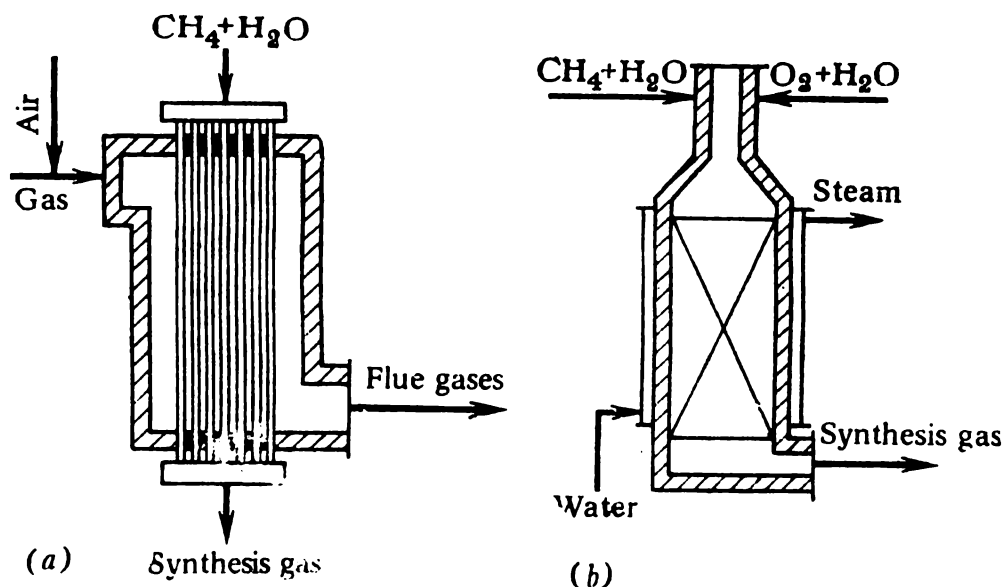


Fig. 1.27. Reactors for catalytic conversion of hydrocarbons:
a—tubular furnace; b—shaft furnace for oxidative conversion.

There is a mixer, into which $\text{CH}_4 + \text{H}_2\text{O}$ and $\text{O}_2 + \text{H}_2\text{O}$ mixtures are introduced. The mixer must provide the homogenization of the mixture under conditions that preclude explosions or ignition. The combustion of methane proceeds 10 times faster than the conversion, which is why the temperature in the upper layers of the catalyst increases rapidly to a maximum (1100-1200 °C) and then falls off down to 800-900 °C) at the outlet from the furnace. As compared with the conversion in tubular reactors, in this technique there is no need for heat-resistant tubes, the design of the reactor becomes very simple and the greater part of its space is efficiently used for the catalyst. In the oxidative conversion the amount of CO in the gas produced increases to a certain extent.

Technology of Catalytic Conversion. The process involves several steps: the preparation of the raw material, conversion, heat utilization, purification of the gas from CO_2 . In the preparation of the feedstock one should keep in mind that the nickel catalyst is susceptible to poisoning by organic sulphur compounds, whose content in the hydrocarbon feedstock is limited to 1 mg of sulphur per 1 m³. The feedstock that does not meet these requirements must be purified, for which purpose it is subjected to catalytic hydrodesulphurization with subsequent removal of the hydrogen sulphide formed. The

feedstock preparation stage includes also the compression of the gas (if necessary), mixing with steam and preheating of the mixture.

Catalytic conversion plants have operated for a long period of time at a pressure close to atmospheric and such plants are still operating at present. The flow diagram of oxidative conversion with a special layout of the reactant mixing, conversion and heat utilization units is shown in Fig. 1.28. Methane (or natural gas) passes through saturation tower 1 which is refluxed by hot water; here it is heated and moistened. It is then mixed with CO_2 , passed into heat exchanger 2, to which an extra amount of steam is introduced, and is

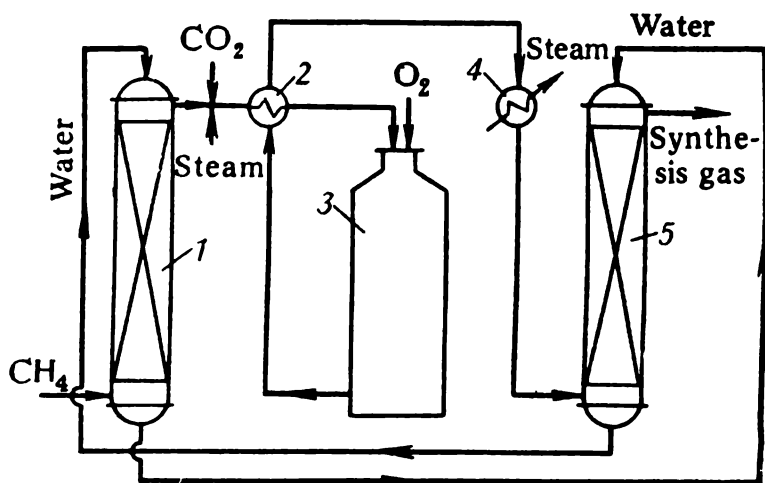


Fig. 1.28. Scheme of oxidative conversion of hydrocarbons at atmospheric pressure:

1—saturation tower; 2—heat exchanger; 3—converter; 4—waste-heat boiler; 5—cooling tower.

heated by the heat of the converted gas. Oxygen diluted with steam is then added to the gas-steam mixture which is run to converter 3, where the reactions described above take place. The heat of the hot gas is used first in heat exchanger 2 and then in waste-heat boiler 4 (to produce steam) and in cooling tower 5 (to heat the water for saturation tower 1). If the conversion is carried out in tubular furnaces, this scheme is somewhat altered, the heat of the hot flue gases being utilized usually for producing steam and preheating the feedstock.

A recent development has been the use of a high pressure, namely 2-3 MPa. Despite the undesirable shifting of the equilibrium, this gives a number of important advantages. First, because of an increase in the reaction rate under pressure the process is considerably intensified, the size of the units and manifolds is reduced, and conditions are provided for developing high-capacity plants. Second, the power consumption is reduced and the heat of the hot gases is used more efficiently. The point is that the syntheses based on CO and H_2 are commonly carried out under pressure and since the volume of the converted gas is larger than the volume of the feedstock, it follows that it is more profitable to compress natural gas with the oxygen

ing already under pressure. The heat utilization systems also become more compact and efficient, and it is possible to use the heat released in the condensation of excess steam from the converted gas, to produce high-pressure steam and to use it for driving the turbocompressors for gas compression. The tendency now is towards the development of power-technological schemes.

The flow diagram of the oxidative conversion of methane (or natural gas) under pressure is given in Fig. 1.29. The methane feedstock purified, if necessary, from sulphur impurities is compressed

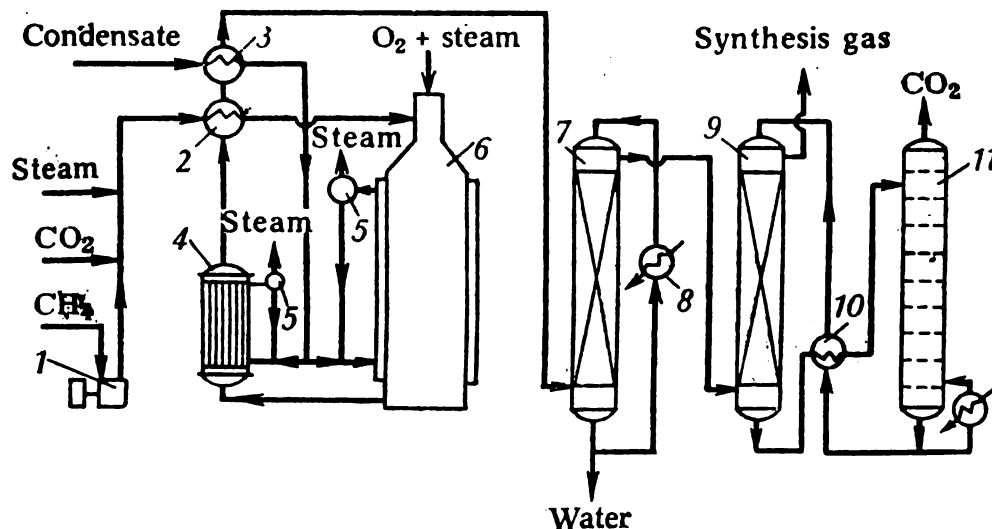


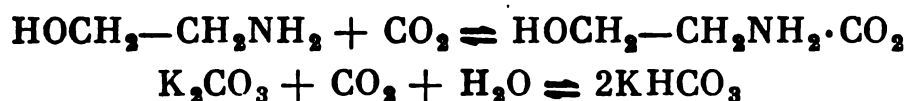
Fig. 1.29. Flow diagram of the oxidative conversion of natural gas under high pressure:

1—turbocompressor; 2, 3, 10—heat exchangers; 4—waste-heat boiler; 5—steam collector; 6—converter; 7—scrubber; 8—cooler; 9—absorber; 11—desorber.

by a turbocompressor 1 up to 2-3 MPa and mixed with a required amount of steam and CO_2 . The mixture is heated in heat exchanger 2 up to 400°C by the partially cooled converted gas and is led to the mixer of converter 6, into which the preliminarily prepared mixture of oxygen with an equal volume of steam is introduced. The converter is cooled by the condensate boiling in the jacket; this produces steam with a pressure of 2-3 MPa, which is separated in steam collector 5. The heat of the hot converted gas leaving the converter at $300-900^\circ\text{C}$ is used in waste-heat boiler 4 to generate high-pressure steam, which is then passed to the steam line of the corresponding pressure or used to drive the turbocompressor. The heat of the partially cooled gas is utilized for preheating the mixture in heat exchanger 2 and also in heat exchanger 3 to heat the water condensate that goes to the waste-heat boiler. The final cooling of the gas is accomplished in scrubber 7 by water that circulates through cooler 8.

The synthesis gas obtained at this stage contains, depending on the requirements for the CO/H_2 ratio, 15-45 percent (by volume) CO , 40-75 percent H_2 , 8-15 percent CO_2 , 0.5 percent CH_4 and 0.5-1 percent each of N_2 and Ar . This gas is purified from CO_2 by using the water absorption under pressure and the chemisorption by an aque-

ous solution of monoethanolamine or potassium carbonate:



Upon heating and pressure reduction the reverse conversions take place and CO_2 is liberated, the solution being regenerated.

The converted gas enters absorber 9, where carbon dioxide is absorbed and the purified gas is delivered to the consumer. The saturated absorbent is heated in heat exchanger 10 by the hot regenerated solution and is led to desorber 11, from the bottom of which the absorbent is passed through heat exchanger 10 back to absorber 9, where CO_2 is absorbed. The carbon dioxide from the top of desorber 11 is compressed to the appropriate pressure and returned to conversion after being blended with natural gas and steam before heat exchanger 2.

The feedstock used to produce 1 m^3 of purified synthesis gas consists of $0.35\text{--}0.40 \text{ m}^3$ of natural gas, 0.2 m^3 of technical-grade oxygen and, depending on the pressure used and the amount of CO_2 added, $0.2\text{--}0.8 \text{ kg}$ of steam.

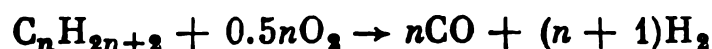
1.5.2. Production of Synthesis Gas by High-Temperature Conversion of Hydrocarbons

The high-temperature conversion of hydrocarbons employs a temperature of $1350\text{--}1450^\circ\text{C}$ and is carried out in the absence of catalysts. The process consists of the incomplete thermal oxidation of methane or liquid petroleum fractions, the basic primary reaction for methane being its oxidation to a mixture of CO , H_2O and H_2 :



There are also formed small amount of CO_2 and (as a result of the pyrolysis reaction) C_3 and C_2 hydrocarbons, including acetylene. The final stage of the process involves the conversion of the remaining hydrocarbons to CO and H_2 by steam, an equilibrium being established between the carbon monoxide and carbon dioxide which is strongly displaced to the formation of CO at a high temperature. Evidently, the decomposition of acetylene leads to the formation of carbon black, which is also capable of being converted by steam ($\text{C} + \text{H}_2\text{O} \rightleftharpoons \text{CO} + \text{H}_2$). The yield of carbon black is particularly significant in the high-temperature conversion of liquid hydrocarbons; in order to lower the yield of carbon black, further steam is added to the feedstock. Thus, this process is analogous in many respects to the oxidative pyrolysis of hydrocarbons to acetylene, the only difference being that the mixture is kept at a high temperature for a relatively long period of time (about 1 s instead of $0.001\text{--}0.01 \text{ s}$). The overall reaction equations in the high-temperature conversion

of methane and liquid hydrocarbons are as follows:



Thus, the H_2/CO ratio may vary from 2 : 1 to 1 : 1, depending on the feedstock. Besides, the gas contains 2-3 percent by volume of CO_2 , 0.3-0.5 percent of CH_4 and up to 1 percent of N_2 and Ar.

The high-temperature conversion of hydrocarbons is carried out at a pressure of 2-3 to 10-14 MPa. The converter used for carrying out

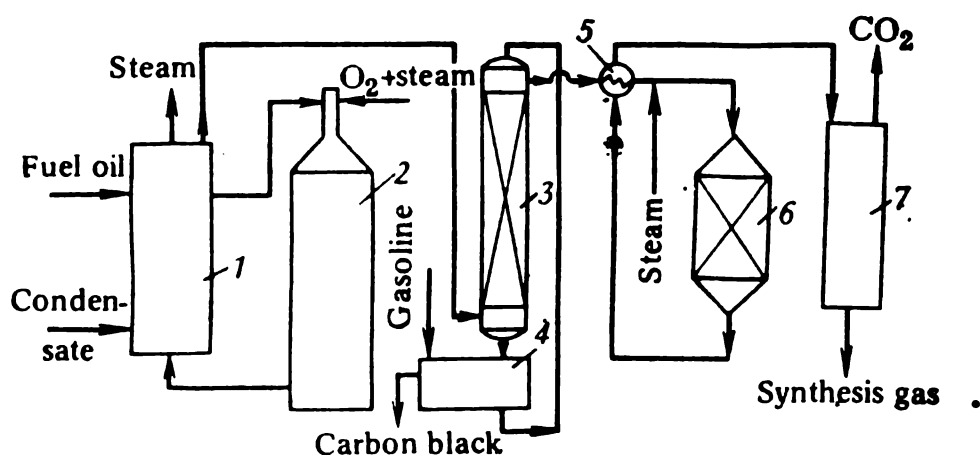


Fig. 1.30. Flow diagram of high-temperature conversion of fuel oil:

1—heat recovery unit; 2—converter; 3—scrubber and carbon-black collector; 4—decanter; 5—heat exchanger; 6—carbon-monoxide converter; 7— CO_2 removal unit.

This process is similar to the one shown in Fig. 1.27b, except that no catalyst is used; this is a hollow apparatus designed for high pressure. The converter has an internal insulation and a water jacket which protect the body from the action of high temperatures, and also a hydrocarbon-oxygen mixer, which provides rapid homogenization of the mixture under conditions that may lead to explosions. The advantages of the process are its high intensity, the design simplicity of the converter, the absence of a catalyst and the possibility of using the feedstock not necessarily of high quality. This accounts for the ever increasing use of the high-temperature conversion, especially in the case of liquid hydrocarbons (including fuel oil and crude petroleum), which is accomplished according to power-technological schemes using high-capacity plants.

The simplified flow diagram of the high-temperature conversion of fuel oil is given in Fig. 1.30. The fuel oil is heated at a pressure of 2-3 MPa and a temperature of up to 500-800 °C in unit 1, where the heat of the hot conversion gases is recovered. This unit consists of heat exchangers and a waste-heat boiler; it may be analogous to the unit shown in Fig. 1.29, except that the converted gases have a higher temperature and contain carbon black. Therefore, the waste-heat boiler is combined with the converter in a single unit and in order

to avoid carbon black deposition, use is largely made of gas-pipe boilers. In such boilers, steam is produced with a pressure of up to 14 MPa and used in power-technological systems.

The preheated fuel oil is introduced through the sprayers into the mixer of converter 2, into which the oxygen-steam mixture is supplied. In the converter jacket, which is required for its body to be cooled, steam is generated, having the same pressure at which the conversion is effected. The hot conversion gases enter heat-recovery unit 1. Then, the carbon black is separated from the gases, for which purpose the gases are most often washed by the circulating water in scrubber 3. The water with carbon black runs into settler 4, into which a light petroleum fraction is introduced, capable of coagulation and extraction of the carbon black from the water layer. The hydrocarbon suspension of carbon black is used in various ways: it is filtered off and burned, the petroleum fraction being returned to the extraction of carbon black; or it may be led in the form of a suspension in fuel oil to conversion. The contaminated water from settler 4 is returned to scrubber 3 for recovery of the carbon black.

After being separated from the carbon black the gas is passed for purification from H_2S and CO_2 , which is carried out by the method described earlier. Not infrequently it is required to alter the H_2 : CO ratio in the gas, increasing the proportion of hydrogen. This is achieved in the unit designed for the conversion of carbon monoxide: the gas is heated in heat exchanger 5 up to 400°C , an appropriate amount of high-pressure steam is added and the mixture is fed to converter 6, where the partial conversion of carbon monoxide over a continuous catalyst bed (iron, chromium and magnesium oxides) is accomplished ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$). The synthesis gas with the required H_2/CO ratio gives up its heat to the gas led to conversion in heat exchanger 5, is purified from CO_2 in unit 7 and is delivered to the consumer.

The production of 1000 m^3 of the $\text{CO} + \text{H}_2$ mixture requires 250 kg of fuel oil (or 380 m^3 of natural gas), $250\text{--}270\text{ m}^3$ of oxygen and 60 kg of steam. In such a process the waste-heat boiler produces $850\text{--}900\text{ kg}$ of high-pressure steam.

1.5.3. Production of Synthesis Gas by Coal Gasification

The gasification of coal was the first process for the manufacture of synthesis gas which was subsequently replaced by the hydrocarbon process. In future, in view of the increasing deficiency and cost of petroleum and natural gas, the process will probably again play an important role in the production of synthesis gas, since it is the most expedient means of processing of coal into chemical products.

The production of synthesis gas from coal is based on the interaction of coal with steam according to the following endothermic

reaction:



The equilibrium of this reaction (known as the water-gas reaction) is shifted to the right at 1000-1100 °C, the reaction velocity being also sufficiently high. When only steam is supplied, the coal is gradually cooled, which is why the process was formerly carried out with the alternation of the steam-blow and coal-heating runs, the coal being heated by its partial combustion during the air-blow run. Later, a continuous method with a steam-oxygen blow came into use; in this process, in the gas generator there simultaneously occurs the exothermic reaction of coal combustion, which provides the required heat balance of the process. Besides, there takes place the conversion of carbon monoxide by steam:



the composition of the gas being close to the equilibrium composition.

The gasification of coal was originally carried out at a pressure close to atmospheric, which did not provide a high capacity of the units. Later, for the same reasons as in the conversion of hydrocarbons, the switch was made to gasification at 2-3 MPa. Two designs of gas generators developed at present are most promising. In the first

(Fig. 1.31a) the process is carried out with a continuous layer of lump coal, which is moving downwards as its lower layers are being burned off. The coal comes in contact with a rising stream of hot gas, providing the most efficient distribution of the various stages of the process along the height of the gas generator and the economic utilization of the heat. The gas in the lower section is first heated by the incandescent residues from gasification; at a higher level, because of the more rapid reaction with oxygen, is the combustion zone, and above this zone are the coal gasification, coking and drying zones. In the second system (Fig. 1.31b), use is made of finely divided coal in the fluidized state in the gas stream. In order to produce a countercurrent of the gas and coal, the gas generator is divided into several sections, in which the corresponding steps take place. All

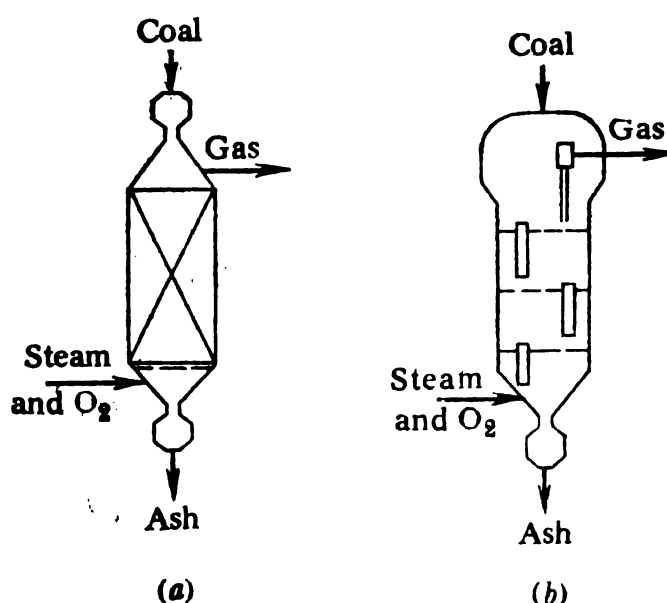


Fig. 1.31. Gas generators for steam-oxygen conversion of coal:

a—gas generator with a continuous layer of small-sized coal; b—sectioned gas generator with a fluidized-bed of coal.

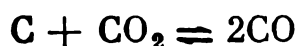
the generators are lined with refractory brick and have a water jacket.

The synthesis gas leaves the generators at 700-800 °C and passes through the heat-utilization system and the system, where it is purified from tars, sulphur compounds and CO₂; finally, it is delivered to the consumer.

The disadvantages of the coal gasification process as compared with the conversion of hydrocarbons are the high cost of the fragmentation and transportation of coal and the more complicated gas purification system. At present, high-capacity plants are being developed, which are equipped with a complex power-technological product-processing and heat-utilization system. As a result, the production of synthesis gas from coal has become more economical and it will probably compete successfully with the hydrocarbon process in the late eighties.

1.5.4. Production of Concentrated Carbon Monoxide

Apart from the synthesis gas, for the manufacture of a number of products there is required concentrated carbon monoxide containing no hydrogen. Carbon monoxide was formerly produced from coke and carbon dioxide under almost the same conditions as synthesis gas:



Today, the most economical process is the separation of synthesis gas with the simultaneous liberation of hydrogen. The difference in the physical properties of CO and H₂ is so great that for their separation one only needs to carry out low-temperature condensation under pressure, using the cold of the fractions obtained, the missing cold being provided by the evaporation of liquid nitrogen. The impurities present in the synthesis gas pass into the carbon monoxide, which is found to contain 3-5 percent (by volume) of CH₄ and N₂ + Ar each.

Another method consists of the extraction of the residual carbon monoxide in the production of hydrogen from synthesis gas:



After being purified from CO₂ the gas contains 2-4 percent (by volume) of CO, which is a catalyst poison in hydrogenation processes. The gas is purified from CO using absorption by aqueous solutions of ammonio-cuprous salts:



When the pressure is reduced and the temperature is raised, carbon monoxide is produced in a concentration of up to 99-99.9 percent. This method of purification from CO has lately been replaced by the more economical hydrogenation of CO to CH₄.

CHAPTER 2

HALOGENATION PROCESSES

In the broad sense, halogenation includes all processes that involve the introduction of halogen atoms into organic compounds. Depending on the halogen, fluorination, chlorination, bromination and iodination reactions are distinguished.

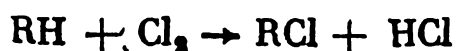
Halogenation is one of the most important processes of organic synthesis. This process is used on a large industrial scale to produce the following compounds: (1) chloro-organic intermediate products (1,2-dichloroethane, chlorohydrins, alkyl chlorides) when the introduction of a sufficiently mobile chlorine atom into the molecule makes it possible to obtain a number of valuable compounds by further transformations of chlorine derivatives; (2) chloro- and fluoro-organic monomers (vinyl chloride, vinylidene chloride, tetrafluoroethylene); (3) chloro-organic solvents (methylene chloride, carbon tetrachloride, tri- and tetrachloroethylene); (4) chloro- and bromo-organic pesticides (hexachlorocyclohexane, chlorine derivatives of acids and phenols). Moreover, halogen derivatives are used as refrigerants (chlorofluoro derivatives, so-called Freons), in medicine (chloral, ethyl chloride), as plasticizers, lubricating oils, etc.

The scale of production of halogen derivatives of hydrocarbons is very large. In the United States, the production forecast for 1980 was about 7 million tons of dichloroethane, more than 3 million tons of vinyl chloride and 300-500 thousand tons of carbon tetrachloride, tri- and tetrachloroethylenes, methylchloroform, and ethyl chloride. Aromatic chloro derivatives, organic fluorine and especially bromine compounds are produced in much smaller quantities.

2.1. General Description of Halogenation Processes

Halogen derivatives are produced by three principal routes: substitution, addition, and decomposition reactions.

Substitution reactions consist of the replacement of atoms or groups by halogen atoms. The most important of these reactions is the replacement of hydrogen atoms:



which can take place at the saturated and unsaturated carbon atoms or in the aromatic ring. The ability to undergo substitution reactions is retained by various derivatives of hydrocarbons.

The replacement of one halogen atom by another is of importance for the preparation of fluoro-, bromo- and iodo-derivative from more available organic chlorine compounds:



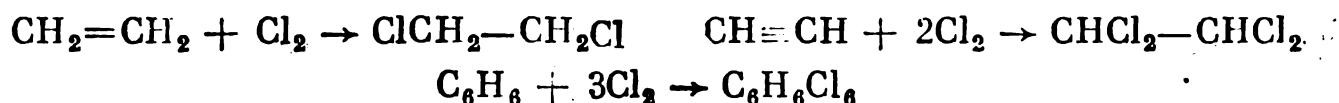
The replacement of the hydroxyl group by a halogen atom is used to obtain some halogen derivatives:



and also acid chlorides:



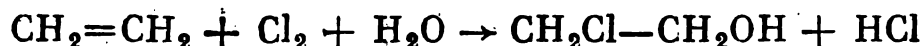
Addition reactions, which consist of the addition of halogenating agents to unsaturated compounds, are of the same great practical importance as substitution reactions. Free halogens are capable of addition across double, triple and aromatic bonds:



Hydrogen halides add on at double and triple bonds (this is the hydrohalogenation reaction):

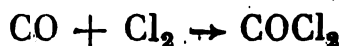


and the olefins also enter into the chlorohydrination or hypochlorination reaction:

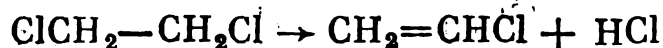


The ability to undergo the above-mentioned addition reactions is retained by many derivatives of unsaturated hydrocarbons.

A special case of chlorination is the addition of a chlorine atom to atoms in their lowest valent state; an example is the synthesis of phosgene from carbon monoxide and chlorine:



Decomposition reactions of chloro derivatives become more and more important. Of these reactions, the dehydrochlorination reaction, which is the inverse of the addition of HCl, takes place most readily:



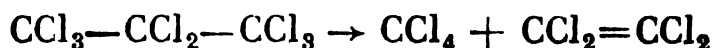
Because of the preferred occurrence of this reaction other decomposition reactions are observed only at high temperatures for perchloro derivatives. Examples are the dechlorination reaction, which is the inverse of the addition of chlorine:



and the decomposition reaction across carbon-carbon bonds which can proceed under the action of chlorine (chlorinolysis):



or at elevated temperature (pyrolysis):



Thermodynamic Description of Halogenation Reactions. Halogenation reactions differ strongly in their energy characteristics, and such differences account for their specific features. Below are compared the heat effects of reactions involving fluorine, chlorine, bromine and iodine for the ideal gas state of substances:

$\text{RCH}_3 + \text{X}_2 \rightarrow \text{RCH}_2\text{X} + \text{HX}$	$-\Delta H_{298}^\circ$ kJ/mol (kcal/mol)
X=F	460 (110)
X=Cl	105 (25)
X=Br	34 (8)
X=I	-50 (-12)
$\text{CH}_2=\text{CH}_2 + \text{X}_2 \rightarrow \text{XCH}_2-\text{CH}_2\text{X}$	
X=F	540 (130)
X=Cl	184 (44)
X=Br	92 (22)
X=I	17 (4)

As can be seen from the figures given above, the reaction heat decreases in the following order: $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$, fluorination and iodination reactions being especially notable. The former are accompanied by the evolution of a large amount of heat, which exceeds the bond dissociation energy of C—C and C—H bonds. If no special measures are taken, this will lead to the complete decomposition of an organic compound, which is why fluorination reactions differ significantly in technology from chlorination reactions and will be considered separately. On the other hand, iodination proceeds with a very insignificant or even a negative heat effect and, in contrast to reactions involving fluorine, chlorine and bromine, is a reversible reaction. This circumstance coupled with the low activity of iodine as a reagent is responsible for the fact that iodine derivatives are usually prepared by other routes. Anyway, iodine derivatives are produced on a small scale and are not the products of basic organic and petrochemical synthesis.

The heat effects of some reactions involving hydrogen halides in the ideal gas state are as follows:

Reaction	$-\Delta H_{298}^\circ$ kJ/mol (kcal/mol)
$C_2H_4 + HF \rightarrow C_2H_5F$	42 (10)
$C_2H_4 + HCl \rightarrow C_2H_5Cl$	71 (17)
$C_2H_4 + HBr \rightarrow C_2H_5Br$	78 (19)
$C_2H_4 + HI \rightarrow C_2H_5I$	78 (19)
$CH_3-CH_2OH + HCl \rightarrow C_2H_5Cl + H_2O$	21 (5)

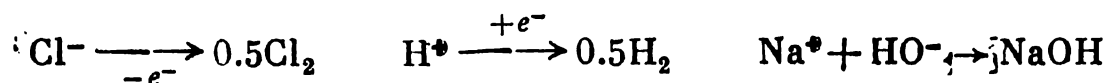
These reactions are all exothermic, the difference in this respect being smaller for hydrogen halides than for free halogens. It is important that all reactions involving hydrogen halides are reversible (their equilibrium characteristics will be described at a later time).

Halogenating Agents. The most important of these are free halogens and anhydrous hydrogen halides. Their boiling points at atmospheric pressure are as follows (in °C):

F_2 . . .	-188.0	HF . . .	19.4
Cl_2 . . .	-34.6	HCl . .	-83.7
Br_2 . .	58.8	HBr . .	-67.0

All these halogenating agents are soluble in organic liquids ($Br_2 > Cl_2 > F_2$ and $HBr > HCl > HF$), which is important when halogenation is carried out in the liquid phase. They have a pungent odour, irritate the mucous membrane of the eyes and the respiratory tracts, and the free halogens have also a suffocating effect. Especially harmful are fluorine and hydrogen fluoride, which cause burns on the skin and the bone tissue.

Chlorine is now made almost entirely by the electrolysis of aqueous solutions of sodium chloride, NaCl (brines), in which hydrogen and sodium hydroxide are formed simultaneously:



The chlorine gas obtained in this reaction has a concentration of about 92 percent Cl_2 and contains N_2 , O_2 and CO_2 as impurities. These impurities can be separated by liquefying the chlorine, whose evaporation gives a pure product, which is often more preferable for chlorination processes.

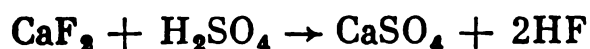
Hydrogen chloride is produced by the high-temperature synthesis from H_2 and Cl_2 :



Fluorine is made by the electrolysis of molten potassium difluoride (KHF_2):



anhydrous hydrogen fluoride is prepared by the action of sulphuric acid on calcium fluoride (fluorspar or fluorite):



All the halogenating agents attack the material of the apparatus, their corrosive action being especially strong even in the presence of traces of moisture. Therefore, the apparatus used for fluorination processes is made of copper or nickel; the steel body of the apparatus employed for chlorination and bromination reactions is protected by linings of lead or ceramic materials; use is also made of special grades of steel, graphite, glass, lead being also used to make tubes. To reduce the corrosion, both halogenating agents and organic reagents must be dried.

Safety in Halogenation Reactions. Apart from the general problems associated with the toxicity and flammability of raw materials (hydrocarbons, carbon monoxide), a number of specific safety problems arise in halogenation processes.

First, not only halogenating agents but the halogen derivatives produced are often highly toxic. They affect the central nervous system, cause a narcotic effect (chloroform, chloral), irritate the mucous membranes of the eyes and respiratory tract (benzyl chloride, chloroacetone); phosgene has a suffocating action. Because of this, halogenation reactions impose increased requirements for the sealing equipment and ventilation. First-aid kits and gas masks must be readily available at working places for the personnel.

Second, free halogens, like oxygen and air, are capable of forming explosive mixtures with hydrocarbons and carbon monoxide. The process of their combustion in the atmosphere of the halogens is highly exothermic and, at certain concentrations, becomes explosive. The lower and upper explosion limits for mixtures of lower paraffins and olefins lie in the range from 5 up to 60 percent (by volume) of hydrocarbon. This calls for special safety measures during the mixing of hydrocarbons with the halogens, especially in high-temperature gas-phase reactions. The explosion hazards of these operations are, however, enhanced by the fact that many of the halogen derivatives form explosive mixtures with air. For instance, the explosion limits of mixtures with air are as follows (in percent by volume):

CH_3Cl	7.6-19.0
$\text{C}_2\text{H}_5\text{Cl}$	3.8-15.4
$\text{C}_2\text{H}_4\text{Cl}_2$	6.2-16.0

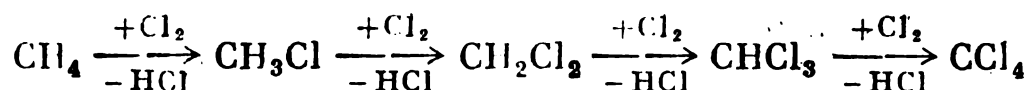
The explosion hazard is reduced with increasing number of halogen atoms in the molecule, and carbon tetrachloride is even used in fire extinguishers.

2.2. Radical-Chain Chlorination

All halogenation processes are classified into two large groups according to their mechanism: radical-chain and ionic-catalytic reactions, which determines their specific physicochemical and technological features.

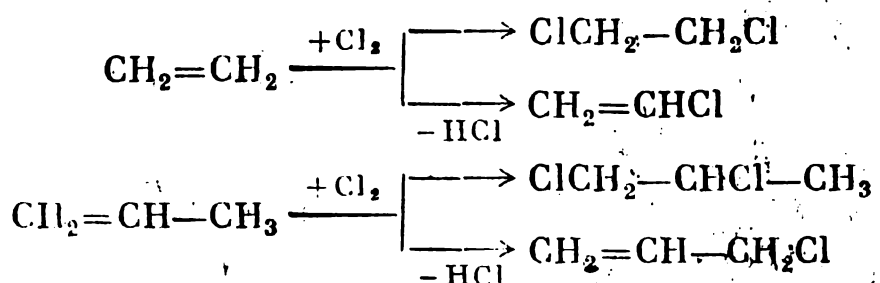
2.2.1. Chemistry and Theoretical Foundations of the Process

Reaction Chemistry. The paraffinic hydrocarbons are capable of only substitution reactions in which hydrogen atoms are replaced by chlorine: several halogen atoms can be inserted one after another into the molecule:



All paraffinic hydrocarbons, including solid paraffin wax and polymers, and also their halogen derivatives (1,2-dichloroethane and others, including polyvinyl chloride) react in this manner.

The olefins undergo chlorination by the radical-chain mechanism predominantly in the gas phase and in the absence of catalysts unsuitable for ionic reactions. Two reactions compete with each other: addition of chlorine at the double bond and the substitution of hydrogen atoms:



It was originally believed that the substitution occurred by way of the addition of chlorine with subsequent elimination of HCl. This viewpoint is, however, rejected by the fact that the substitution of propylene and elimination of HCl from 1,2-dichloropropane yield products of different composition. Thus, the substitution and addition reactions are two independent routes in the chlorination of olefins. The degree of each of these reactions depends on temperature: the higher the temperature the more selective is the substitution and vice versa. This can be clearly seen from Fig. 2.1, which shows graphically the effect of temperature on the direction of the gas-phase chlorination of propylene. Other olefins that are not branched at the unsaturated carbon atom behave in an analogous manner. In each of them there is a certain "critical" chlorination temperature at which the substitution begins to prevail over the addition reaction.

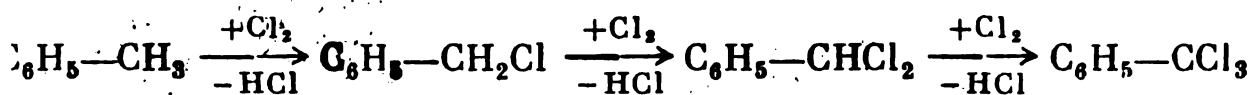
creases with lengthening of the carbon chain in the olefin and is from 270 to 350 °C for ethylene, from 250 to 300 °C for propylene, from 170 to 200 °C for 2-butene, etc. Olefins such as isobutylene undergo only substitution reactions.

As a result of the competition between substitution and addition reactions, the chlorination of olefins may involve the replacement of hydrogen at various positions in the molecule. The substitution reaction occurs preferentially at the most reactive allyl position and only to a small extent at unsaturated carbon atoms.

Because of this, the chlorination of propylene by substitution yields 96 percent of allyl chloride ($\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}$) and only 4 percent of monochloropropylenes ($\text{CHCl}=\text{CH}-\text{CH}_3$, $\text{CH}_2=\text{CCl}-\text{CH}_3$). Another reaction consists of the successive replacement of hydrogen atoms, just as is the case with the chlorination of paraffins.

Aromatic hydrocarbons undergo chlorination by the radical-chain mechanism in the absence of catalysts used for ionic reactions — FeCl_3 , AlCl_3 , and also of the corresponding metals, which limits the choice of materials for the reaction apparatus.

As with olefins, aromatic hydrocarbons give three types of halogen compounds: side-chain substituted halogen compounds, nuclear substituted compounds, and substances in which halogen adds on to the C—C bond of the aromatic ring. For benzene homologues, at all permissible temperatures the side-chain substitution is the most preferential; it proceeds successively as follows:



If the side chain is longer, the substitution takes place predominantly at the α -position relative to the aromatic nucleus; an example is the chlorination of ethylbenzene which gives α -chloroethylbenzene, $\text{C}_6\text{H}_5-\text{CHCl}-\text{CH}_3$.

The chlorination of benzene homologues at low temperatures (30 °C) gives a large number of by-products formed by way of the addition of chlorine at the C—C bonds of the nucleus, while the side-chain substitution becomes more and more appreciable with increasing temperature. Since the side-chain chlorination occurs more

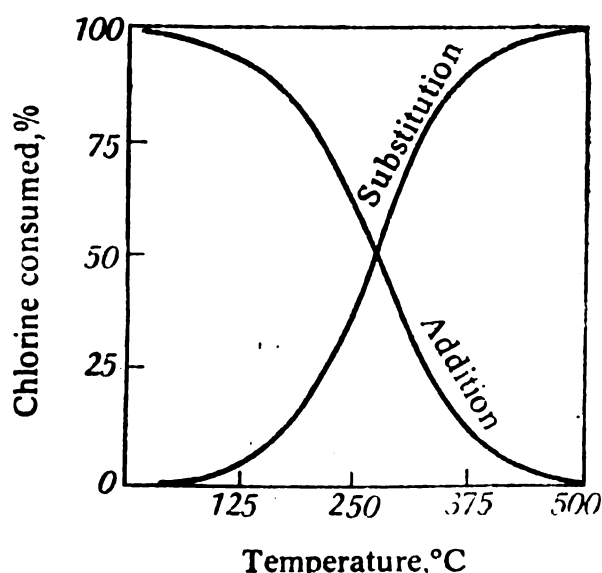
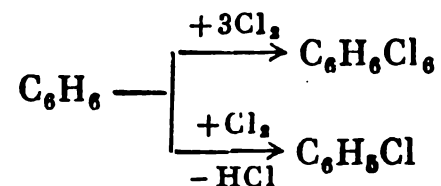


Fig. 2.1. The ratio of addition and substitution reactions upon chlorination of propylene.

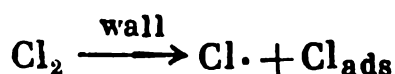
preferentially, the last two processes are observed in pure form only for aromatic compounds having no side chains. At a low temperature from benzene there is formed hexachlorocyclohexane and at a high temperature the product is chlorobenzene:



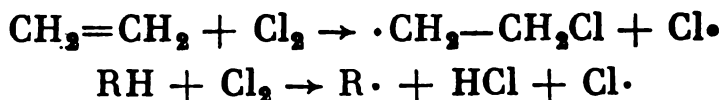
Here again successive chlorination reaction is possible with the remaining hydrogen atoms being replaced by chlorine atoms.

Reaction Mechanism and Kinetics. The processes under consideration belong to unbranched chain reactions which proceed via the intermediate formation of free atoms and radicals.

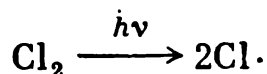
Chain initiation is accomplished by several routes. In the thermal gas-phase chlorination it is effected by the splitting of the chlorine molecule into atoms with the participation of the wall or packing which facilitates the cleavage of the Cl—Cl bond due to chemisorption



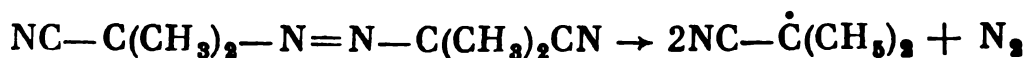
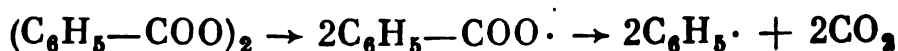
However, in certain cases of thermal chlorination the reaction started at moderate temperatures (100-150 °C), which are insufficient for a simple bond cleavage in the chlorine molecule. It is presumed that the formation of free atoms and radicals here is favoured by the interaction of chlorine with an organic substance which lowers the endothermicity of this step:



In a photochemical chlorination reaction, the cleavage of the chlorine molecule is achieved by the absorption of a quantum of energy, say upon irradiation with ultraviolet light (mercury-quartz lamps):



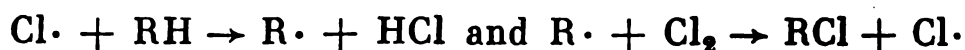
Finally, upon chemical initiation of the process there are added special initiators—substances capable of decomposing into free radicals at moderate temperatures. The most frequently used initiators are benzoyl peroxide and azobisisobutyronitrile (Porofor):



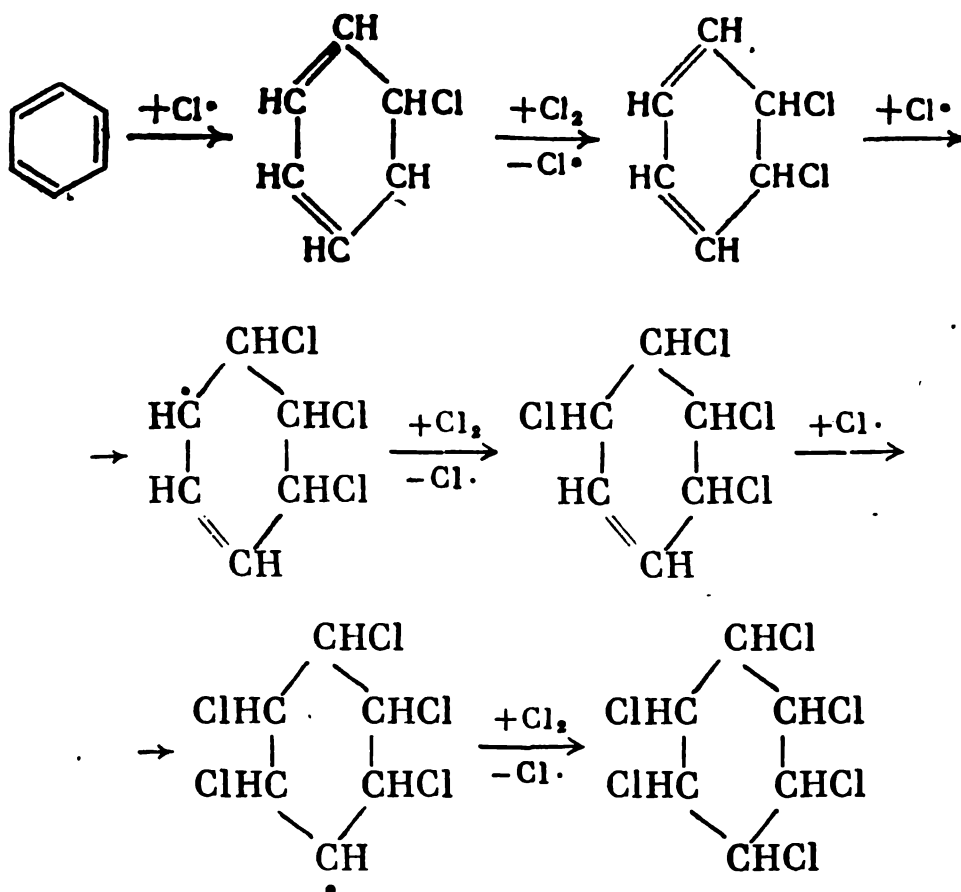
The free radicals formed interact with the chlorine molecule to give free chlorine atoms:



Chain propagation proceeds with the aid of the chlorine atoms formed as a result of chain initiation. In substitution reactions the chain step consists of two recurring elementary reactions:

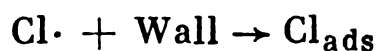


The addition, say across aromatic bonds, occurs as follows:



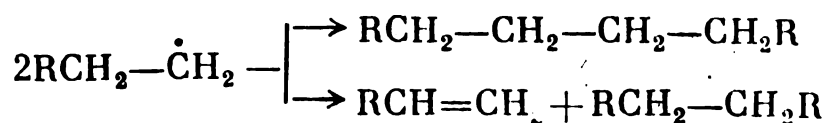
The length of the reaction chain, i.e., the number of chain steps in it, may reach several ten thousands upon chlorination of especially pure compounds. In practical conditions, when technical substances are used, the chain is usually composed of several hundreds of steps.

Chain termination during the course of gas-phase chlorination takes place on the reactor wall or on the packing:

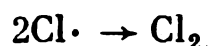


apart from this linear termination, in gas-phase reactions there are observed cases of quadratic termination, which are especially characteristic of liquid-phase processes. Depending on the bond dissociation energy in organic compounds and on the stability of intermediate radicals, quadratic termination proceeds on hydrocarbon radicals

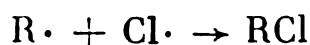
(the chlorination of hydrocarbons, notably, toluene):



on chlorine atoms (the chlorination of chloro derivatives):



or, in some instances, in a crossed manner:



Finally, chain termination may take place on inhibitors; the compounds used as inhibitors are phenols, sulphur compounds, and also other hydrocarbons that form more stable free radicals. Especially important is the inhibiting action of oxygen ($\text{R}\cdot + \text{O}_2 \rightarrow \text{ROO}\cdot$), which is usually contained in chlorine gas as an impurity. This inhibiting action manifests itself up to 350 °C; above this temperature it becomes insignificant.

Depending on the mode of chain initiation and termination, the chlorination may be described by various kinetic reaction equations. In the gas phase the reaction is most often first-order with respect to reagents:

$$r = k[\text{RH}][\text{Cl}_2]$$

For liquid-phase chlorination three types of kinetic equations have been predominantly observed:

$$r = k[\text{I}]^{0.5}[\text{Cl}_2] \quad r = k[\text{I}]^{0.5}[\text{RH}] \quad r = k[\text{I}]^{0.5}[\text{RH}]^{0.5}[\text{Cl}_2]^{0.5}$$

where $[\text{I}]$ is the initiator concentration or the irradiation intensity.

In the presence of inhibitors the rate of reaction becomes inversely proportional to their concentration, for example,

$$r = k[\text{Cl}_2]^2[\text{O}_2]^{-1}$$

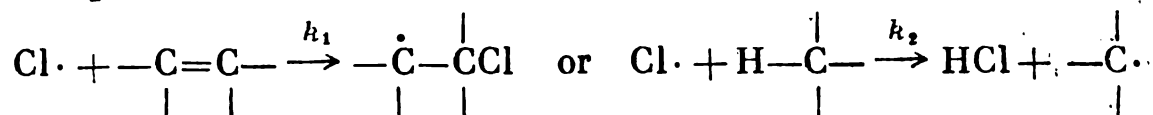
From this it follows that for radical-chain chlorination it is necessary to use as pure compounds as possible, including chlorine containing no oxygen, i.e., produced by the evaporation of liquid chlorine.

The differences in activation energy between various methods of chlorination depend on the chain-initiation step. The activation energy is 126 to 168 kJ/mol (30-40 kcal/mol) for thermal chlorination, about 84 kJ/mol for chemical initiation, and 21 to 42 kJ/mol for a photochemical reaction. The process upon thermal chlorination can be intensified only by increasing the temperature; upon chemical initiation this can be achieved by increasing the temperature and initiator concentration; in photochemical reactions, which are practically unaffected by temperature, the process can be intensified by increasing the irradiation intensity.

Apart from thermal, photochemical and chemical initiation, there is also a catalytic (or thermocatalytic) method of carrying out the

rocess, which makes use of heterogeneous catalysts (activated carbon, etc.). In the presence of such catalysts the activation energy is lowered and chlorination proceeds at a temperature which is 100–50 °C lower than for thermal processes. The mechanism of action of these catalysts is, however, still unclear.

Parallel Reactions upon Chlorination and the Selectivity of the Process. It has been said above that the radical-chain chlorination of olefins and aromatic hydrocarbons involves parallel addition and substitution reactions. The degree of each of these reactions depends on the relative of the elementary step of interaction of a free chlorine atom at the corresponding position of the molecule of an organic compound:



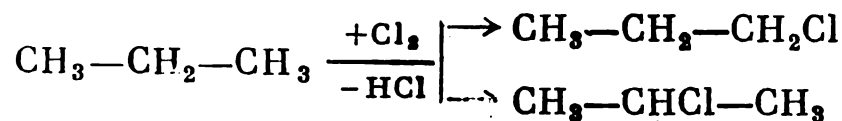
With the molecularity of both reactions being the same, the selectivity depends only on the ratio of the rate constants of these steps which is determined by the difference in activation energy and by the temperature:

$$S_1 = \frac{1}{1 + k_2/k_1} = \frac{1}{1 + \frac{k_{2,0}}{k_{1,0}} \exp\left(-\frac{E_2 - E_1}{RT}\right)}$$

The addition of chlorine across an unsaturated or aromatic bond is energetically more favourable than the hydrogen-atom abstraction and has a lower activation energy. Therefore, the addition is favoured by a decrease in temperature, while the substitution reaction is assisted by an increase in temperature; the curves obtained

for the yield of the products are similar to those shown in Fig. 2.1.

In turn, substitution can also occur at various positions in the molecule; this also refers to the chlorination of paraffins; an example is the preparation of 1- and 2-chloropropanes from propane:



Here, the selectivity and composition of the products obtained also depend on temperature and the difference in activation energy

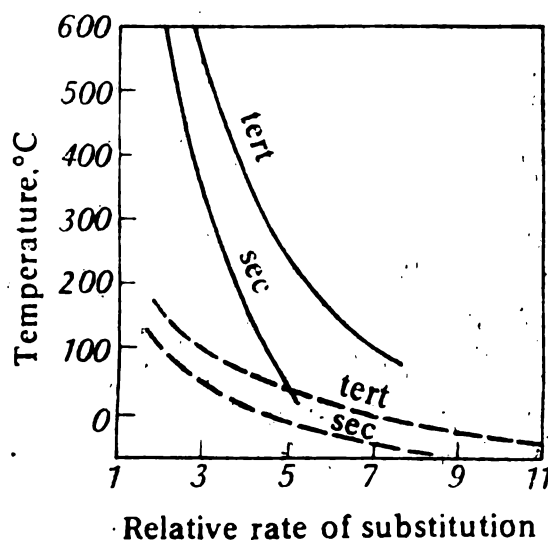
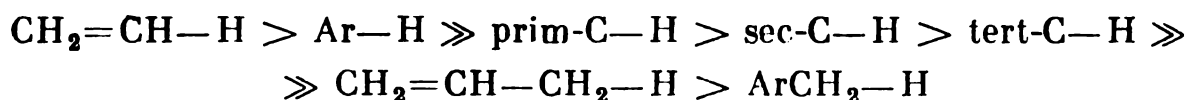


Fig. 2.2. Temperature dependence of the relative rate of substitution of various hydrogen atoms for the chlorination of paraffins. Solid lines = gas phase; dashed lines = liquid phase.

between the corresponding steps of hydrogen-atom abstraction, i.e., on the energy of the C—H bonds being broken. These energies increase in the following sequence:

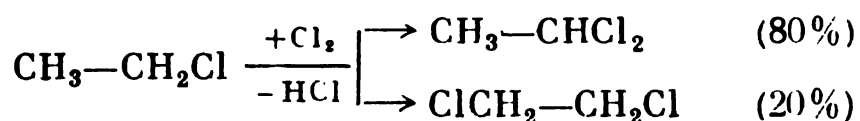


which determines the inverse order of the relative reactivity of various hydrogen atoms upon their replacement. This accounts for the fact that the radical-chain substitution at unsaturated and aromatic carbon atoms proceeds only at high temperatures, and the substitution at the allylic position of olefins and in the side chain of aromatic hydrocarbons is most preferable. The dependence considered above also holds for the chlorination of paraffins, as can be seen from Fig. 2.2, which shows the reactivity of various hydrogen atoms with respect to the atom that is in the primary position; its reactivity is assumed to be equal to unity. The relative rates of substitution are brought closer with increasing temperature and depend, in addition, on whether the reaction is carried out in the liquid or gas phase. From these data one can calculate the composition of monochloro derivatives that can be obtained in the chlorination of any paraffinic hydrocarbon:

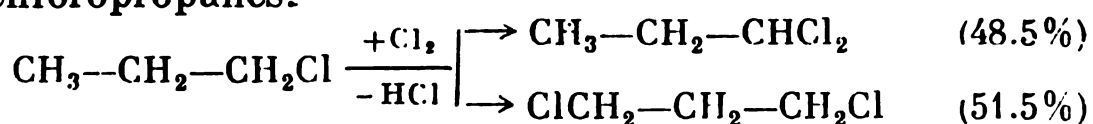
$$N_i = \frac{n_i R_i}{n_{\text{pri}} + n_{\text{sec}} R_{\text{sec}} + n_{\text{tert}} R_{\text{tert}}}$$

where N_i is the mole fraction of a given monochloroparaffin; n_i is the number of hydrogen atoms in the molecule, whose replacement leads to the formation of the chloroparaffin; R_i is the relative reactivity of various hydrogen atoms.

If there is chlorine in the molecule, the reactivity is generally lowered. In such a case, the hydrogen atoms at the adjacent carbon atom are deactivated most strongly. The deactivating action of chlorine is reduced for more remote positions in the molecule and affect little the hydrogen atoms that reside at the carbon atom bearing the chlorine atom. As a result, the chlorination of ethyl chloride gives mainly 1,1-dichloroethane:



and the chlorination of 1-chloropropane yields a mixture of 1,1- and 1,3-dichloropropanes:

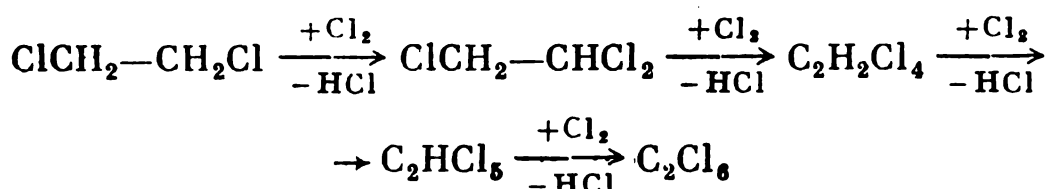


Apart from the temperature and the phase (liquid or gas) in which the reaction is carried out, the selectivity of radical-chain chlorination reactions is also influenced by the state of the chlorine atom in

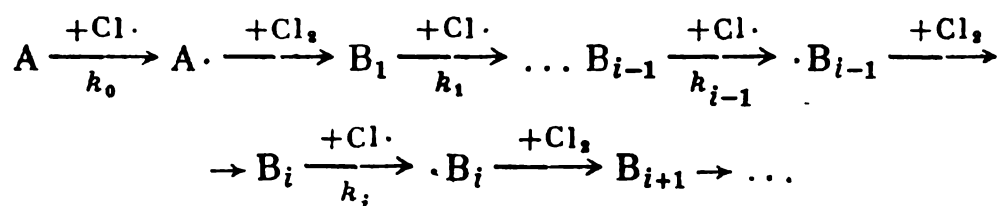
solution. Some solvents (*o*-dichlorobenzene, hexachlorobutadiene) form complexes with chlorine, lower its activity and, hence, increase the selectivity with respect to the attack on the various positions in the molecule. This also allows the composition of the products of parallel chlorination reactions to be controlled.

It should be noted that radical-chain chlorination is nevertheless only slightly selective. Therefore, an organic reagent must be sufficiently pure (98 percent purity and higher) in order to avoid excessive consumption of chlorine and contamination of the products.

Consecutive Chlorination Reactions and the Selectivity of the Process. Apart from parallel reactions, radical-chain chlorination almost always involves consecutive-parallel conversions, as a result of which an ever increasing number of chlorine atoms is introduced into the molecule. As a further example (in addition to those given above) may be cited the chlorination of 1,2-dichloroethane:



The composition of the products of successive chlorination is also determined by the elementary step of the attack of chlorine on starting compound and the chlorination products:



Since these steps are bimolecular, the expression for the ratio of the products (differential selectivity) will be as follows:

$$-\frac{d[\text{B}_i]}{d[\text{A}]} = \frac{k_{i-1} [\text{Cl}\cdot] [\text{B}_{i-1}] - k_i [\text{Cl}\cdot] [\text{B}_i]}{k_0 [\text{Cl}\cdot] [\text{A}]} = \frac{k_{i-1} [\text{B}_{i-1}] - k_i [\text{B}_i]}{k_0 [\text{A}]}$$

The introduction of chlorine atoms leads to the deactivation of the molecule, which is why the ratio of the rate constants of the consecutive steps (k_i/k_{i-1}) for radical-chain chlorination processes is smaller than unity and usually varies from 0.2 to 0.8. It means that the sequential introduction of chlorine atoms into the molecule is increasingly complicated. An exception is methane, whose specific structure (with four hydrogen atoms) is responsible for the slower (than in all other cases) first step of its chlorination.

Just as with all other consecutive-parallel reactions, the composition of chlorination products is governed by the ratio of the reactants, namely the ratio of the chlorine that has entered into the reaction to the starting organic substance. These dependences are shown in

Fig. 2.3 for two cases. Similar dependences are observed for other radical-chain chlorination reactions. It can be seen that nearly in all cases a mixture of products of varying degree of chlorination is obtained and that the maximum of the yield of each of them is observed

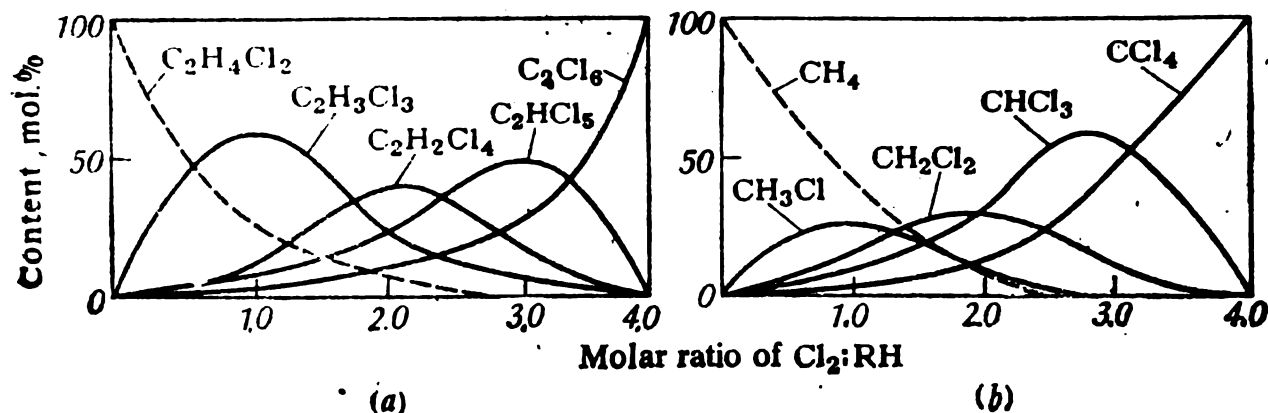


Fig. 2.3. Dependence of the composition of the chlorination products on the ratio of the reagents:

a—chlorination of 1,2-dichloroethane; *b*—chlorination of methane.

approximately at the same ratio of the reactants that corresponds to the stoichiometry of the formation of a given product from Cl_2 and RH .

From the graphs of the composition of the products we can plot the curves for the selectivity of the reaction for any compound

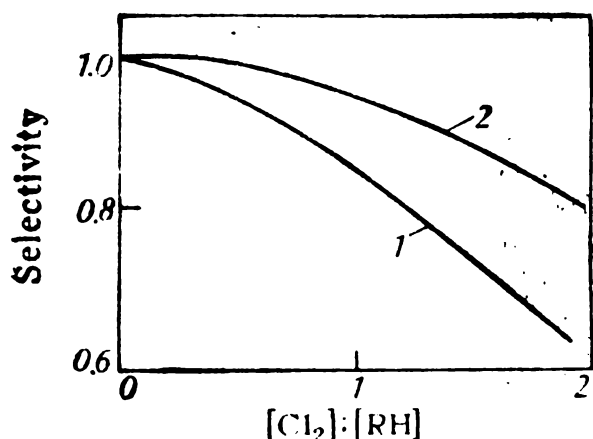


Fig. 2.4. Dependence of the selectivity on the molar ratio of converted chlorine to paraffin or chloroalkanes:

1—first substitution product; 2—second substitution product, the intermediate being recycled.

(Fig. 2.4.). For the first substitution product (curve 1) the selectivity falls off with increasing $\text{Cl}_2:\text{RH}$ ratio. If the end products are the subsequent chlorination products, the selectivity with respect to them can be increased by recycling a compound with an insufficient degree of chlorination to the reaction (for example, CH_3Cl in the production of CH_2Cl_2 from methane). In this case, if we neglect the losses, the selectivity will also decline with increasing molar ratio of $\text{Cl}_2:\text{RH}$ (curve 2).

The choice of the optimal ratio of the reactants is governed by economical factors. A comparison is made of the energy consumed for the regeneration and recycling of a large excess of unreacted organic reagent to the reaction and the increased consumption of the raw material with a decrease in the selectivity of the process when this excess is not large. The optimal ratio of the reactants does not correspond to the maxima of the curves in Fig. 2.3: it is equal to

(0.1-0.2) : 1 for the preparation of the first product and to (0.3-0.5) : 1 for the preparation of the second product [the excess of the organic substance with respect to chlorine is equal to (5-10) : 1 or (3.3-2) : 1, respectively]. When the succeeding chlorination product is also of practical value, the optimal ratio of the reagents is altered by increasing the amount of chlorine. When perchloro derivatives are to be produced, use is even made of an excess of chlorine with respect to its stoichiometric amount in order to ensure more complete substitution.

Finally, a further factor which can substantially raise the selectivity of the reaction is the choice of the reactor type. As with other consecutive reactions, the highest selectivity is achieved, other conditions being equal, by using continuous plug-flow reactors and batch reactors. Therefore, under continuous conditions the reactor design should be made as close to the plug-flow model as possible.

2.2.2. Technology of Liquid-Phase Chlorination

For the liquid-phase radical-chain chlorination carried out at relatively low temperatures (from 40 to 100-150 °C) initiators are always required or the mixture must be irradiated, which leads to additional money expenditure as compared with thermal chlorination. The choice of liquid-phase chlorination is therefore justified for the production of thermally unstable compounds, which readily lose HCl (monochloroparaffins with a long carbon chain, C_2 and higher polychlorides) and also compounds for which thermal chlorination is less selective. Moreover, liquid-phase chlorination is preferred in cases where more than two or three chlorine atoms are to be introduced, when a high heat of reaction often does not allow the process to be conducted in the gas phase because of low heat-transfer coefficients.

2.2.2.1. Products Obtained by Liquid-Phase Chlorination

The method of radical-chain liquid-phase chlorination is used to produce many products.

Polychloro Derivatives of Ethane. *1,1,2-Trichloroethane*, Cl_2CH-CH_2Cl , is a liquid with a boiling point of 113.9 °C. It is prepared from 1,2-dichloroethane with 1,1,2,2- and 1,1,1,2-tetrachloroethanes formed as by-products. It is used for the production of a valuable monomer, vinylidene chloride ($CH_2=CCl_2$).

1,1,1-Trichloroethane or *methylchloroform*, CH_3-CCl_3 , is a liquid with a boiling point of 74.1 °C; it is prepared from 1,1-dichloroethane with 1,1,2-trichloroethane and tetrachloroethane formed as by-products. It is an excellent solvent and is produced on a large

scale. Another route to 1,1,1-trichloroethane is the hydrochlorination of vinylidene chloride.

Pentachloroethane, $\text{CCl}_3\text{—CHCl}_2$, is a liquid with a boiling point of 186.8°C ; it is synthesized by the chlorination of 1,2-dichloroethane or 1,1,2,2-tetrachloroethane. It is used for the production of a valuable solvent—tetrachloroethylene, $\text{CCl}_2=\text{CCl}_2$.

Hexachloroethane or *carbon hexachloride* $\text{CCl}_3\text{—CCl}_3$, is a crystalline compound (subl. p. 185.6°C). It is prepared by the exhaustive chlorination of any chloroethanes. Hexachloroethane is used for the manufacture of trifluorotrichloroethane, $\text{Cl}_2\text{CF—CF}_2\text{Cl}$ (a solvent) and especially of trifluorochloroethylene, CClF=CF_2 (a monomer) and Freons.

Chloroparaffins. These compounds are commercially produced in several grades, which are used for various purposes. *13-Chloroparaffin* containing 12-14 percent of chlorine is produced from the kerosene or narrower fraction ($\text{C}_{12}\text{—C}_{16}$) of paraffin-base petroleum and also from a mixture of *n*-paraffins derived from the corresponding fractions. It is a *sec*-monochloroalkane containing an impurity of the primary isomer and dichloro derivative. The compound is used for the synthesis of a surfactant of the alkylaryl sulphonate type.

Liquid chloroparaffins contain 40-49 percent chlorine and are used as plasticizers (especially for polyvinyl chlorides) and as additives to lubricating oils.

Solid chloroparaffin contains 70-72 percent chlorine and is used as an additive to plastics and synthetic rubbers to render them fire-resistant. The last two products are blends of polychlorinated compounds; they are produced by the chlorination of soft or solid paraffin wax.

Chlorinated polymers are manufactured in several grades and find various applications. They include chlorine rubber, chlorinated polyethylene, polypropylene and polyvinyl chloride with a chlorine content of up to 70 percent. The introduction of chlorine usually increases the elasticity of the polymers and its adhesion to various materials.

Products of Chlorination of Aromatic Hydrocarbons. *Benzyl chloride*, $\text{C}_6\text{H}_5\text{—CH}_2\text{Cl}$, is a liquid with a boiling point of 179.3°C and is used for the introduction of the benzyl group into various compounds, which leads to the formation of benzyl cellulose, benzyl esters, benzyl alcohol, benzyl cyanide, butylbenzyl phthalate (a plasticizer), etc. Benzyl chloride is prepared by the chlorination of toluene with benzal chloride ($\text{C}_6\text{H}_5\text{—CHCl}_2$), benzotrichloride ($\text{C}_6\text{H}_5\text{—CCl}_3$) and chlorotoluenes ($\text{ClC}_6\text{H}_4\text{—CH}_3$) formed as by-products.

p-Xylylene dichloride, $\text{ClCH}_2\text{—C}_6\text{H}_4\text{—CH}_2\text{Cl}$, is produced by the chlorination of *p*-xylene and used for the synthesis of thermally stable polymers.

Hexachloro-m- and *hexachloro-p-xylenes*, $\text{Cl}_3\text{C}-\text{C}_6\text{H}_4-\text{CCl}_3$, are crystalline compounds; they are prepared by the chlorination of the *m*- and *p*-xylenes, respectively. These compounds are used for the production of acid dichlorides of isophthalic and terephthalic acids $[\text{C}_6\text{H}_4(\text{COCl})_2]$, which result from the hydrolysis of hexachlorides by water. Besides, hexachlor-*p*-xylene is a medicinal preparation.

1,2,3,4,5,6-Hexachlorocyclohexane or *hexachlorane*, $\text{C}_6\text{H}_6\text{Cl}_6$, is prepared by the additive chlorination of benzene with hepta- and octachlorocyclohexanes formed as by-products. The technical product is a mixture of eight isomers, of which only the γ -isomer is an active insecticide (it is a crystalline solid, m.p. 112-113 °C). Its content in the technical product is only 11-18 percent, which is why the γ -isomer is concentrated by extraction; this gives enriched hexachlorane containing 80-90 percent of the γ -isomer and Lindane or Gammexane (the 99-percent γ -isomer). The other isomers are processed to trichlorobenzene by dehydrochlorination. Hexachlorane is a widely used versatile insecticide.

2.2.2.2. Reaction Conditions and Reactor Types

Liquid-phase chlorination is carried out by bubbling gaseous chlorine through the liquid reaction mass. Chlorine dissolves in it and the reaction proceeds in solution. In many cases, the liquid medium is the organic reactant itself, which is used in large excess in order to avoid deeper chlorination. The products formed are accumulated in this reagent and the density of the mixture increases, this being used for the control of the degree of conversion. When liquid polychloroparaffins and hexachloroxylenes are to be produced, the composition of the liquid phase varies during the course of the reaction until a viscous or molten product containing no starting reagent is formed. Finally, in the production of solid polychloroparaffins and chlorinated polymers, solvents (carbon tetrachloride, *o*-dichlorobenzene) are used to attain a better homogenization of the mixture, but some polymers are chlorinated in aqueous or other suspensions.

Both chemical and photochemical methods of initiation are used in industry. The first method has the advantage of being carried out in a simple reaction unit but is associated with additional expenditure on a rather expensive initiator. In the second method, the reactor design is substantially complicated, the investment cost and power consumption increase, but no initiator is used and the compounds synthesized are not contaminated by its decomposition products. The choice of the method is governed by economical factors. Moreover, there is at least one example, where the reaction in the liquid phase proceeds at 120-150 °C without an initiator and irradiation, i.e., by the most economical thermal route—this is the initial step of chlorination of higher paraffins.

Apart from the ratio of the reactants, which has been considered above, the choice of temperature and initiator concentration or radiation intensity is important.

In photochemical chlorination, the choice of temperature is not restricted since it has practically no effect on the reaction rate. Nevertheless, it is more profitable to use water cooling, which is why the photochemical synthesis of hexachlorocyclohexane is conducted at 40-60 °C.

When chemical initiators are used, the choice of temperature is governed by a sufficiently high rate of their decomposition — the temperature is 70-100 °C for azobisisobutyronitrile and 100-120 °C for benzoyl peroxide. In such cases, the temperature and the initiator concentration are interconnected. First, with an average chain length the initiator concentration must not be lower than the number of gram-atoms of chlorine introduced per 1 litre of reaction mass divided by the doubled chain length (since each molecule of the initiator gives rise to two chains). Second, the chain length itself upon its quadratic termination is inversely proportional to the square root of the chain initiation rate and decreases with increasing temperature and initiator concentration. As a result, the consumption of the initiator per unit amount of product is expressed by a differential equation:

$$\frac{d[I]}{d[B]} = A[I]^{0.5}e^{-E/2RT}$$

where I is the initiator; E is the activation energy of its thermal decomposition; B is the product; A is a proportionality coefficient. Thus, in order to reduce the consumption of the initiator the temperature and the initiator concentration must be lowered, which is profitable but leads to a decrease in the reaction rate and increased investment cost for the reaction unit; this requires the optimization of the process conditions with respect to economic criteria. Moreover, the consumption of the initiator can be reduced by introducing it periodically in small portions (in batch processes) or along the reactor length (in continuous processes) and also by changing the temperature as the initiator is being consumed. What has been said also refers to photochemical chlorination reactions, when the increase of the irradiation intensity and of the reaction rate leads to a shortening of the chain length and an increase in power consumption. The optimum in both cases is shifted to the side of the relatively low process intensity.

The reaction unit (just as the entire process of liquid-phase chlorination) can be made of either batch- or continuous action type. In either case, the main apparatus (the chlorinator) must be equipped with a bubbler for chlorine, coolers for the removal of the heat evolved, a reflux condenser or a gas separator in the off-gas (HCl) line,

and by various manifolds and control and measuring devices. The reactor used for photochemical chlorination is additionally equipped with devices for the irradiation of the reaction mass (internal mercury-quartz lamps protected by domes or external lamps, which illuminate the reactor through the glass "windows" in the reactor body). Typical reactors for liquid-phase radical-chain chlorination are shown schematically in Fig. 2.5.

The first reactor (Fig. 2.5a) is designed for batch processes and is a hollow bubbling column which is cooled externally. Circulation

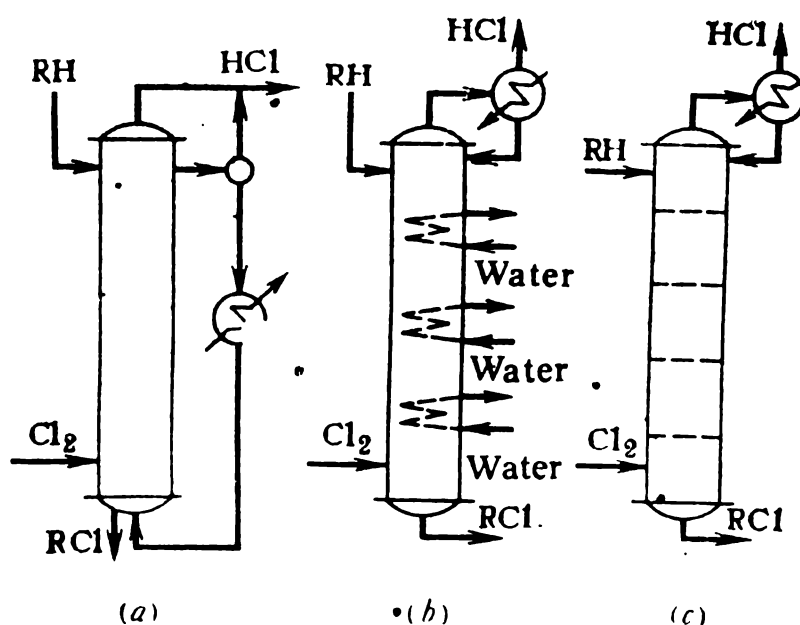


Fig. 2.5. Basic types of chlorinators for liquid-phase radical-chain chlorination: a—externally cooled batch chlorinator; b—internally cooled continuous chlorinator; c—continuous chlorinator with heat removal by evaporation.

the reaction mass through the cooler is accomplished by means of pump or by way of natural circulation (due to the difference in density between the relatively hot column liquid, which is filled with gas bubbles, and the colder liquid, in the circulation circuit which contains no gas). Polychloroparaffins are produced in this way. When polymers are chlorinated in solution, the reaction heat can be removed by way of the evaporation of the solvent, which is condensed and returned to the reactor through the reflux condenser. The continuous variant of the externally cooled reactor is not suitable because of the intensive stirring of the mixture and the decrease of the selectivity. For this reason, continuous reactors are built as a bubbling column with internal cooling (Fig. 2.5b) by means of coils (sometimes with the aid of a water jacket) or with a reflux condenser. The liquid and the gas usually move countercurrently, and in order to reduce the lateral mixing and to raise the selectivity it is useful to divide the reactor into sections by building a series of trays along its height or by setting up a series of reactors.

When low-boiling substances (say, 1,2-dichloroethane, 1,1-dichloroethane) are to be chlorinated, the heat evolved can be removed by evaporation of these substances in an HCl current. Here, internal cooling proves useless and is replaced by a reflux condenser (Fig. 2.5c).

2.2.2.3. The Process Stages

The technology of liquid-phase radical-chain chlorination involves several stages: the preparation of the reagents, the chlorination proper, the processing of the off-gas and the utilization of HCl, the refining of the liquid reaction mass and the recovery of the reaction products.

The *feed preparation stage* usually consists of the evaporation of liquid chlorine and its heating to a temperature close to room temperature. Sometimes, organic reagents are not preliminarily subjected to special purification and are pumped directly into the reactor. If they contain moisture, the evaporated chlorine is dried with sulphuric acid and the organic reagent by azeotropic distillation of water or using solid adsorbents. In some cases, purification from metals or their salts, which catalyze ionic reactions, is required, and the chlorine is filtered off from the scale and the organic reagent is subjected to distillation. Finally, if the organic reagent contains sulphur compounds (or other inhibitors), hydrodesulphurization is carried out.

The processing of the effluent gas consists primarily of the recovery of the vapours of the starting organic reagent, this being accomplished by cooling with brines or by absorption with a solvent (the best solvent to be used for this purpose is a higher-boiling by-product formed in this particular process). When nonvolatile substances are to be chlorinated (say, soft or solid paraffin wax), it will suffice to cool the gas by water. Then, the HCl is absorbed from the gas. Additive chlorination yields little hydrogen chloride, in which case the gas is washed with water, which is removed as sewage. In substitutive chlorinations, the amount of HCl formed is large and it is subjected to water absorption to give 20-30 percent of hydrochloric acid. The gas left is discharged into the atmosphere.

The refining of the liquid reaction mass consists of the purification from the dissolved HCl and the recovery of the products. The purification from HCl is effected using several methods (Fig. 2.6). When low-volatile substances (such as chloroparaffins, benzyl chloride, hexachlorane, chloroxylenes) are produced, the HCl is blown off in a column by nitrogen or air (Fig. 2.6a). In other cases, the common procedure is to wash the liquid in extraction columns with water, aqueous caustic and again with water in the countercurrent flow of the phases (Fig. 2.6b). This leads to the formation of a considerable amount of waste waters. In more modern plants, HCl is distilled

gether with the excess reagent in a fractionating column (Fig. 2.6c) with subsequent condensation of the liquid, its recycling, and removal of the HCl into the off-gas line. The schemes that exclude washing are the most advanced.

After the HCl is removed the major product is sometimes obtained ready for use (polychloroparaffins); there is only required the crystallization (hexachloroxylenes) or steam distillation of the solvent, fractionation or crystallization (chlorinated polymers, hexachlorocyclohexane). In other cases, fractional distillation is carried out, whereby

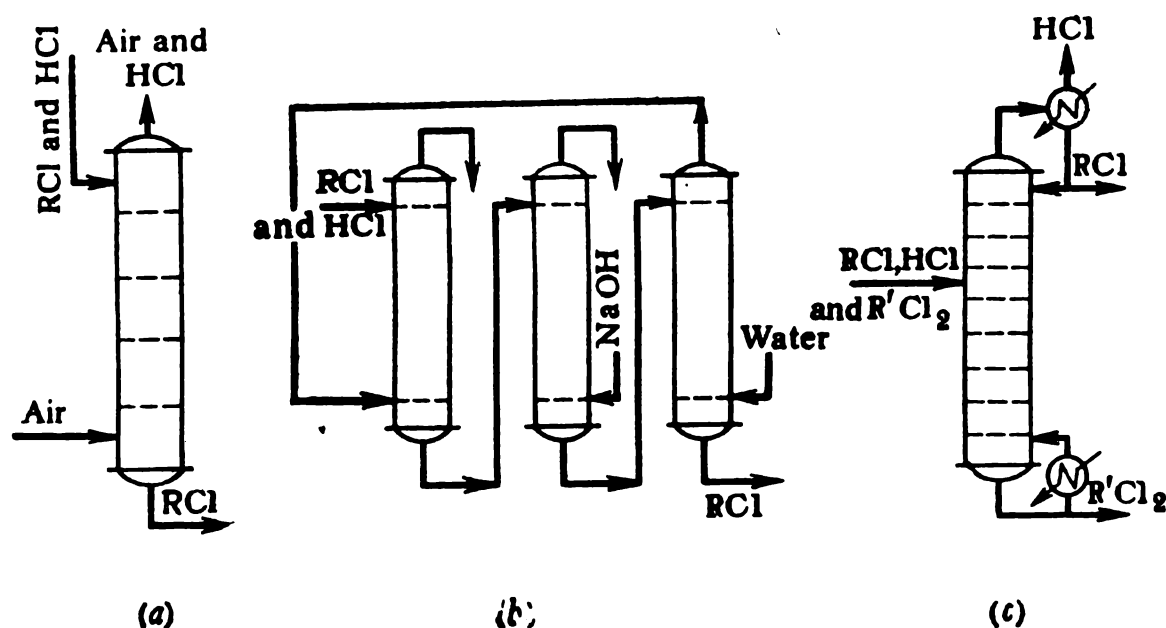


Fig. 2.6. Flow diagrams of purification of chlorination products from hydrogen chloride:

a—blowing of HCl by air (dry neutralization); b—extraction of HCl by water and aqueous NaOH (wet neutralization); c—distillation of HCl together with excess reagent (dry neutralization).

the unconverted organic reagent, end product and by-products are separated (the synthesis of ethane chlorides and benzyl chloride).

The flow diagram of the liquid-phase radical-chain chlorination will be described below for the synthesis of methylchloroform from 1,1-dichloroethane (Fig. 2.7); it is used, almost without modifications, for the production of 1,1,2-trichloroethane from 1,2-dichloroethane.

A solution of Porofor of the required concentration in 1,1-dichloroethane is prepared in one of the collectors 1. The resulting solution is continuously pumped into the upper part of chlorinator 3, gaseous chlorine being introduced at the bottom. In order to maintain the low-boiling 1,1-dichloroethane in the liquid state, a pressure of 0.2-0.3 MPa is required.

The chlorinator is fitted internally with trays and the heat evolved is removed by evaporation of 1,1-dichloroethane in reflux condenser 4, from which the condensate runs back into the reactor. Because of the volatility of the mixture being lowered during the movement of the liquid from the top to the bottom of the column an optimal tempera-

covered for the production of vinylidene chloride and tetrachloroethylenes can be used for the manufacture of trichloroethylene or other organic products.

Technology of Gas-Phase Chlorination

1. Gas-Phase Chlorination Products

Gas-phase chlorination is used to produce a small number of products, namely chloro derivatives of methane, allyl and methallyl chlorides, and dichlorobutylenes.

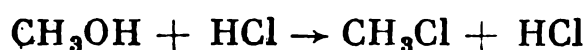
The chloro derivatives of methane are of great practical value. *Methyl chloride* or *monochloromethane*, CH_3Cl (at atmospheric pressure it is a gas which is condensed at -23.7°C) is used as a methylating agent in the manufacture of dimethyldichlorosilane, $(\text{CH}_3)_2\text{SiCl}_2$, other methylsilanes, methyl mercaptan, CH_3SH , etc.

Ethylene dichloride or *dichloromethane*, CH_2Cl_2 (a liquid boiling at 39.8°C) is used as a solvent.

Chloroform or *trichloromethane*, CHCl_3 (a liquid, b.p. 61.2°C) is used for the production of monochlorodifluoromethane, CHClF_2 (used as a refrigerant) and tetrafluoroethylene, $\text{CF}_2=\text{CF}_2$, which is a valuable monomer.

Carbon tetrachloride, CCl_4 (a liquid, b.p. 76.5°C) is used as a solvent, a component of some pesticides and chiefly for the production of freons (CCl_2F_2 and CCl_3F).

All these derivatives can be produced by the chlorination of methane in the form of mixtures of varying composition. But the preferred route to methyl chloride is the hydrochlorination of methanol:

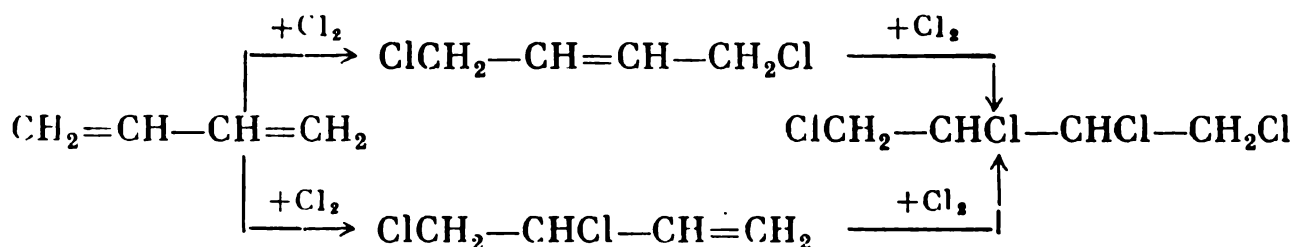


Methanol yields a purer product. Moreover, it has been suggested that methyl chlorides of methane be also obtained from methanol via methyl chloride by chlorination of the latter in the gas phase. No deep refrigeration is needed for the separation of methane from chloro derivatives. More economical processes have been developed for the manufacture of carbon tetrachloride, based on the chlorinolysis of organic wastes.

Allyl chloride, $\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}$, and *methallyl chloride*, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}_2\text{Cl}$, are liquids with boiling points of 45.0 and 72.2°C , respectively. The former is widely used to introduce allyl groups into various compounds (the synthesis of allyl esters, allylamines, allyl alcohol) and, especially, for the production of epichlorohydrin, which is used in the synthesis of epoxide polymers and glycerine. Dichlorides, which are formed as by-products in the chlorination of propylene, are used as pesticides known as the DD preparation. Methallyl chloride is a pesticide and is also used to introduce the methallyl group, espe-

cially in the production of methallyl sulphonate, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}_2\text{SO}_2\text{ONa}$. Allyl and methallyl chlorides are obtained by gas-phase chlorination of propylene and isobutylene, respectively.

Dichlorobutylenes—*1,4-dichloro-2-butene*, $\text{ClCH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$, and *1,2-dichloro-3-butene*, $\text{ClCH}_2-\text{CHCl}-\text{CH}=\text{CH}_2$, are obtained, in distinction to the preceding products, by the radical chain additive chlorination in the gas phase. The feedstock is butadiene; first, a mixture of dichlorobutylenes is obtained, and then the double bond becomes saturated with formation of tetrachlorobutane.



In order to suppress the last reaction, an excess of butadiene with respect to chlorine is required, just as with other consecutive-parallel reactions. Besides, substitution products are formed, but the yield is not large because of the relative slowness, of this side reaction.

Dichlorobutylenes assume industrial significance as intermediates in organic synthesis. The 1,4-isomer is the basic feedstock for the production of adipodinitrile, $\text{NC}-(\text{CH}_2)_4-\text{CN}$, hexamethylenediamine, $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$, and adipic acid, $\text{HOOC}-(\text{CH}_2)_6-\text{COOH}$, which are used for the manufacture of polyamide fibre. The 1,2-isomer is readily converted to chloroprene, $\text{CH}_2=\text{CCl}-\text{CH}=\text{CH}_2$, this route being the basis for the most modern, efficient method of synthesis of this important monomer. The chlorination reaction gives a mixture of the two isomers, but they are capable of being reversibly isomerized to each other in the presence of zinc or copper salts as catalysts. In this way, with the isomerization step being added to the chlorination reaction, it is possible to obtain any of these isomers as the end product.

2.2.3.2. Process Conditions and Reactor Types

In spite of the absence or weak inhibiting action of oxygen, gas phase chlorination nevertheless makes use of chlorine obtained by the evaporation of liquid chlorine, since with the unconverted hydrocarbon being recycled the inert impurities of the electrolytic chlorine gas are rapidly accumulated to intolerable amounts.

An important factor is the choice of the temperature and reactant

tio. In the production of allyl and methallyl chlorides the end products are those into which one chlorine atom is introduced, which is why the process is carried out in the presence of an excess of the corresponding hydrocarbons, this excess being not too large, since the chlorides also find application. If the molar ratio of hydrocarbons to chlorine is 5 : 1 in the synthesis of allyl chloride and 2 : 1 in the production of methallyl chloride, the yield of these chloro derivatives amounts to 80 percent; the excess hydrocarbon is separated and returned to the reaction cycle. In the production of allyl chloride, the choice of temperature is governed by the high selectivity of the substitution reaction as compared with addition (see Fig. 2.1), and the reaction is conducted at 500-520 °C. With methallyl chloride, when the extent of the addition reaction is insignificant, the process is accomplished at 150-200 °C. Finally, the synthesis of dichlorobutylenes is carried out at about 300 °C and with an excess of butadiene.

When methane is chlorinated, the end products are methylene chloride, chloroform or their mixtures with carbon tetrachloride. When methylene chloride is the desired product, the molar ratio of methane to chlorine is about 4 : 1, the unconverted methane and ethyl chloride being recycled. With chloroform as the major end product the molar ratio of CH_4 to Cl_2 is about 0.8 : 1; the unconverted methane and CH_3Cl are recycled and, apart from chloroform, there are also obtained methylene chloride and carbon tetrachloride. The chlorination of methane is accomplished either thermally at 400-550 °C or thermocatalytically at 350-400 °C.

Chlorination in the gas phase is always carried out at atmospheric pressure and continuously by passing a mixture of reagents through the chlorinator. An important operation is the mixing of the reactants, which must provide the instantaneous homogenization of the mixture. Special mixers are used for this purpose, say tangential-type mixers, in which turbulent mixing is effected.

The reactors for gas-phase chlorination are of three basic types (Fig. 2.8). The common features are the protection of the steel body (against high temperature and corrosion) by ceramic lining and the isothermal nature of the process. The latter is achieved as follows: the heat evolved in the reaction is consumed to heat the mixture to the required temperature and to offset the losses into the surroundings. Depending on the thermal balance of the process, the reactants fed to the chlorinator must be cold (in the synthesis of methane polyhalides, when the heat of reaction is very high) or preheated (in the production of allyl chloride).

In the first case, for thermal chlorination use is made of the chlorinator of type *a*, in which the cold reactants are rapidly heated by the hot packing, which plays the role of a heat accumulator. In thermocatalytic chlorination, the same effect is achieved due to the heated particles of the fluidized bed of the catalyst or refrigerant

(Fig. 2.8b); for strongly exothermic syntheses of methane polychlorides, the temperature can be controlled by injection of liquid CCl_4 . In both cases, a considerable lateral mixing of the mixture is observed but in the production of methane chlorides this is not so important

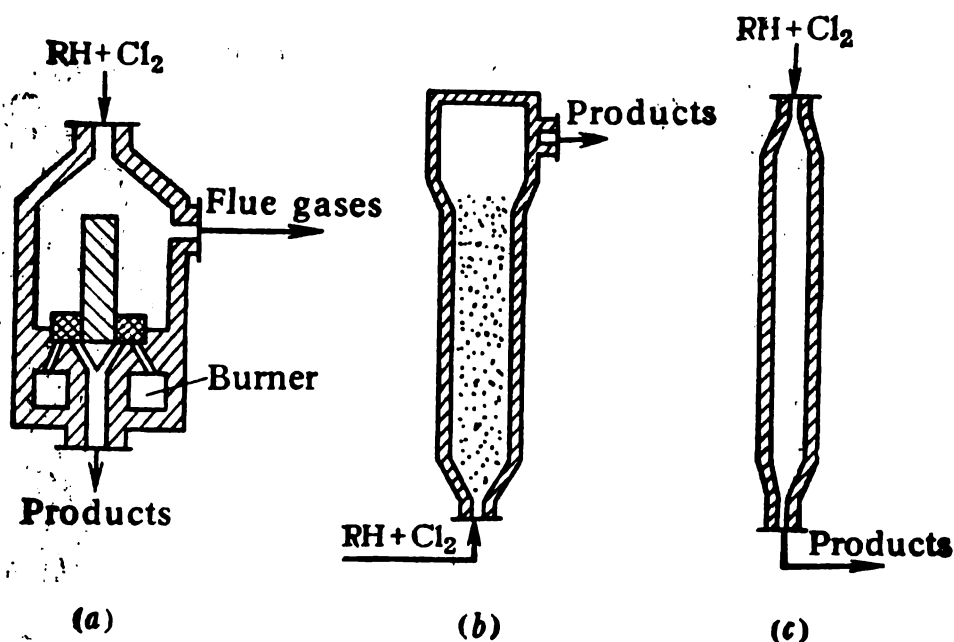


Fig. 2.8. Basic types of reactors for liquid-phase chlorination:

a—with a packing heat carrier; b—with a fluidized-bed of heat carrier (catalyst); c—for processes with preheating of the mixture

because they are all of practical value. When the preheated reactants are fed into the chlorinator (the synthesis of allyl chloride), the reaction may start even in the mixer, and the chlorinator is made as a hollow tube with a considerable height-to-diameter ratio (Fig. 2.8c)

The contact time in various chlorination processes ranges from 0.1 to 2 s.

2.2.3.3. The Steps of the Process

The technological scheme of gas-phase chlorination involves the same steps as in liquid-phase chlorination. The preparation of reactants consists of the evaporation of liquid chlorine, the preheating of gaseous chlorine, the drying of the reactants with concentrated sulphuric acid or adsorbents, the mixing of the reactants with one another and with the recycle. In the synthesis of allyl and methallyl chlorides the feed hydrocarbons are vaporized and heated to a required temperature.

After the reaction is complete the mixture is purified from HCl and the end products are separated from the substances to be recycled. Two basic schemes are employed to achieve this purpose:

(1) if the condensation of the products is complicated (as in the synthesis of methylene chloride in a large excess of methane), the entire mixture is first freed from HCl with formation of 30-percent

hydrochloric acid and then compressed and dried, the gaseous recycle being separated and the liquid products subjected to fractional distillation;

(2) when simple condensation of the reactants is possible, they are first separated from the recycle and HCl and then subjected to fractional distillation. The gaseous mixture is purified from HCl and the cycle is dried and returned to the reaction cycle.

The flow diagram of the production of allyl chloride is given in Fig. 2.9. Liquid chlorine is vaporized in unit 1 and its vapours are

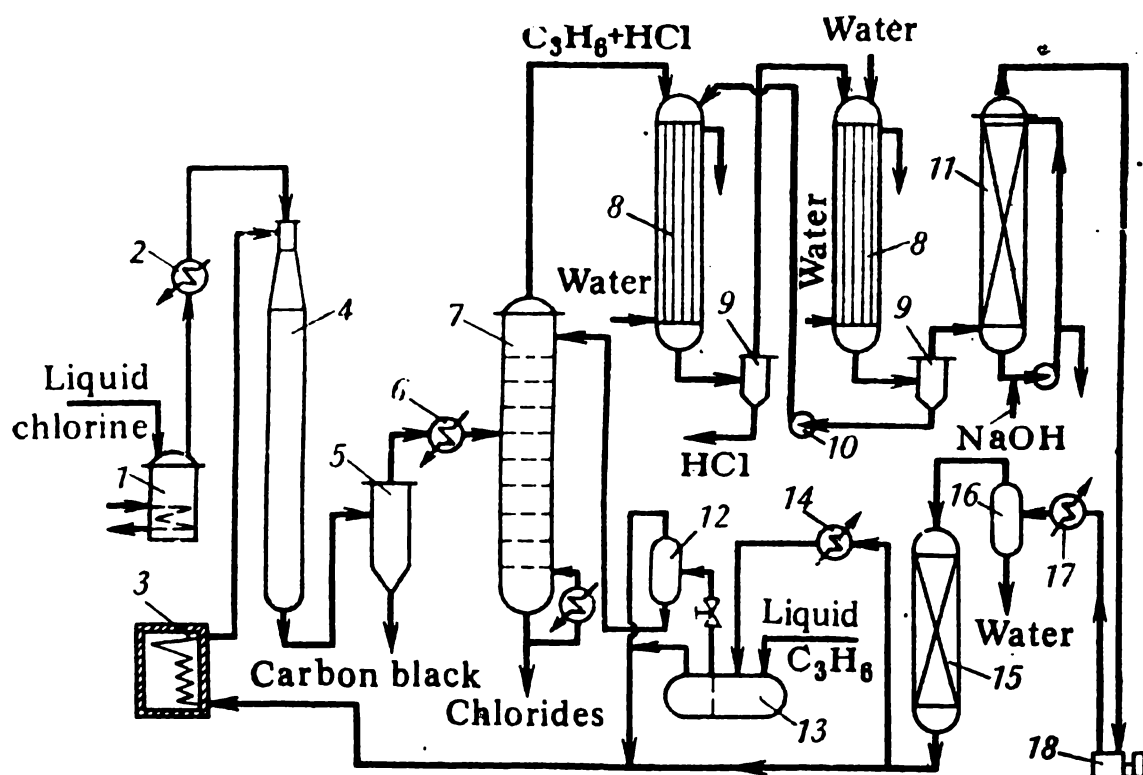


Fig. 2.9. Flow diagram of allyl chloride production:

1—vaporizer; 2—heater; 3—tubular furnace; 4—chlorinator; 5—cyclone; 6, 17—coolers; 7—stripping and condensation column; 8—film absorbers; 9, 12, 16—separators; 10—circulation pumps; 11—caustic scrubber; 13—liquid propylene tank; 14—condenser; 15—adsorber-drier; 18—compressor.

lightly heated in heater 2, after which they are passed through the flow meter into chlorinator 4. Propylene is heated up to 350 °C in tubular furnace 3 and led to the upper part of the chlorinator, which plays the role of the mixer. The hot reaction gases pass through cyclone 5, where coke and carbon black are separated, and cooler 6, where steam can be obtained, following which they are led to stripping-condensation column 7. This column is refluxed by liquid propylene, the evaporation of which cools the gas, from which all the chloro derivatives are completely condensed.

The propylene and hydrogen chloride from the top of column 7 are passed to absorption of hydrogen chloride, which gives concentrated hydrochloric acid. Figure 2.9 shows the scheme of film absorption in graphite shell-and-tube absorbers 8, in which the heat of absorption is removed by water, this making it possible to produce more con-

centrated hydrochloric acid. In each of absorbers 8 the gas and water (or hydrochloric acid) move together downwards, but at the same time their countercurrent contact also takes place, this being effected by supplying water into the last (in the direction of movement of the gas) absorber and the weak acid into the first. The gas leaving the second separator 9 is additionally purified from HCl in caustic scrubber 11, and the unconverted propylene is compressed by compressor 18 to 1.5-2 MPa.

The compressed propylene is chilled in cooler 17 and the condensed water is separated from it in separator 16, after which the gas is subjected to drying in adsorber 15 over Al_2O_3 (as a matter of fact, there are 2 or 3 batch driers, in which adsorption, blowing, and desorption with the heated gas and again blowing are successively carried out). Part of the dry propylene in the gas state is throttled and passed into tubular furnace 3, from which it is sent to the reaction. The remainder is condensed in unit 14 and collected in tank 13. The liquid propylene is throttled, as a result of which it is cooled and partially vaporized. These vapours together with the gas from tank 13 are mixed with the propylene that goes to the reaction and the liquid propylene is used to reflux column 7.

A fresh propylene fraction may be led, depending on its pressure, state of aggregation and the extent of drying, to the various points of the process. The liquid dry fraction is introduced under pressure into tank 13. During circulation inert impurities accumulate in the gas; in order to prevent excessive dilution a small portion of the gas is exhausted into the atmosphere. The mixture of the chloro derivatives from the still of column 7 is sent for fractional distillation (not shown in the flow diagram). The allyl chloride is separated from the more volatile chloropropylenes and higher-boiling dichlorides, as a result of which it is produced as a technically pure product.

2.3. Ionic-Catalytic Halogenation

Such processes include the addition of halogens across double and triple bonds, the chlorohydrination of olefins, hydrochlorination reactions, nuclear substitution and the chlorination of some oxygen-containing and nitrogen compounds.

2.3.1. Additive Halogenation by Free Halogens

2.3.1.1. Addition of Halogens at Unsaturated Carbon-Carbon Bonds

We have already described the addition of chlorine to olefins in the gas phase which proceeds by a radical-chain mechanism. If this involves the formation of a liquid phase, the process is sharply speed-

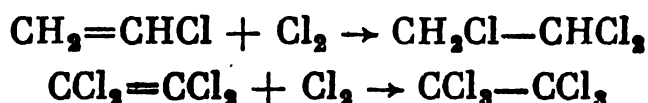
gas, which is used in all the processes described above. Addition of catalysts not only speeds up the addition reaction but also increases its selectivity. As a result of the joint action of oxygen and catalyst, the yield of the substitution by-product in the chlorination of ethylene drops from 10 to 0.5-2 percent.

Products Obtained by Addition of Halogens. The highest-tonnage product is *1,2-dichloroethane*, $\text{ClCH}_2\text{—CH}_2\text{Cl}$ (a liquid, b.p. 83.5°C). It is produced by addition of chlorine to ethylene and is used for the manufacture of monomers—vinyl chloride, $\text{CH}_2=\text{CHCl}$, and vinylidene chloride, $\text{CH}_2=\text{CCl}_2$, ethane and ethylene polychlorides (especially, the solvents tri- and tetrachlorethylenes, $\text{CHCl}=\text{CCl}_2$ and $\text{CCl}_2=\text{CCl}_2$) and also ethylene diamine, $\text{H}_2\text{NCH}_2\text{—CH}_2\text{NH}_2$, polysulphide rubbers, Thiokols $(\text{—CH}_2\text{—CH}_2\text{—S}_x\text{—})_n$ and a number of other products. 1,2-Dichloroethane is also present in some fumigants.

1,2-Dichloropropane, $\text{ClCH}_2\text{—CHCl—CH}_3$ (a liquid, b.p. 98.6°C) is produced by chlorination of propylene. It is used as a fumigant and also for the synthesis of polysulphide rubbers.

1,2-Dibromoethane and *1,2-dibromopropane* are produced by a process analogous to those used for the manufacture of chloro derivatives from ethylene and propylene, respectively. Along with ethyl bromide, they are used for the preparation tetraethyl lead solutions, which are added to motor fuels to raise their octane number.

1,1,2-Trichloroethane and *hexachloroethane* have recently been synthesized not by radical-chain substitution of 1,2-dichloroethane but by the more economical and more selective addition of chlorine to the corresponding chloro-olefins:



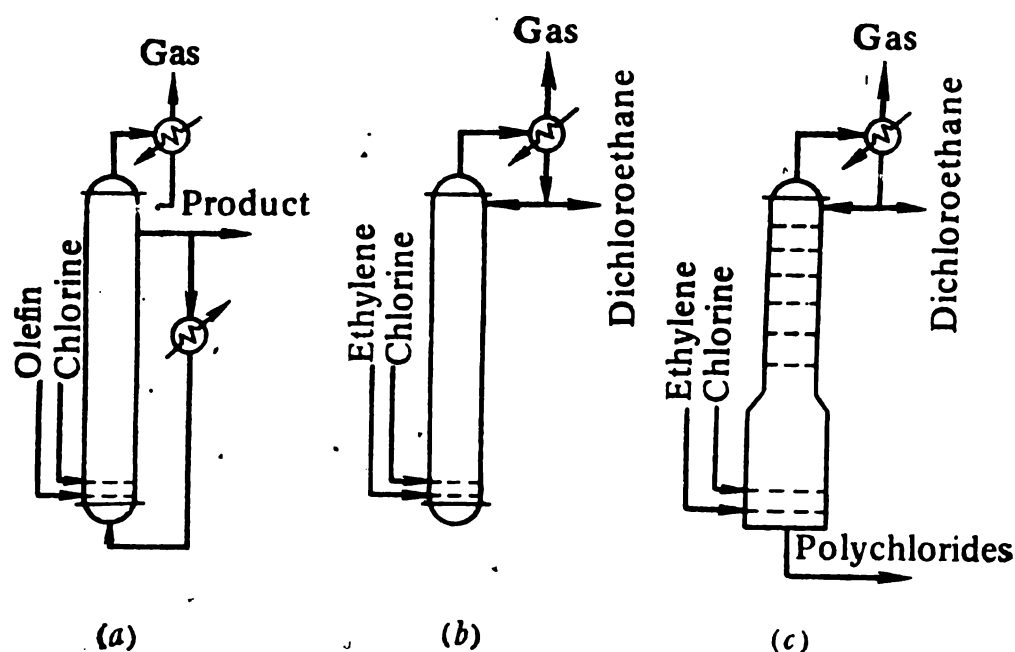
1,1,2,2-Tetrachloroethane, $\text{CHCl}_2\text{—CHCl}_2$, is obtained by chlorination of acetylene and used for the production of trichloroethylene, a solvent. Because of the high cost of acetylene, this method is not promising and is superseded by more efficient methods of processing of less costly ethylene via 1,2-dichloroethane.

Technology of the Process. The reactions considered above are noted for their high selectivity and velocity, and the reactants must not necessarily be pure. For example, not infrequently use is made of diluted chlorine gas left after the liquefaction of chlorine or of olefin fractions containing the corresponding paraffins or inert impurities (but not other olefins). But the drying of the gases is here a requisite too.

The process is accomplished by bubbling the gaseous reactant through the liquid product, in the solution of which the interaction takes place. Formerly, in order to avoid substitution, the temperature was maintained as low as possible (30°C), but heat removal limited the capacity of the reactor. Today, the process is conducted at $70\text{--}100^\circ\text{C}$

order to suppress substitution use is made of the inhibiting oxygen and catalysts. The catalyst used is specially prepared FeCl_3 or iron blocks, which are placed in the reactor and which FeCl_3 under the influence of chlorine. The ratio of the organic to chlorine taken here is close to the stoichiometric ratio with a small excess of the olefin (about 5 percent) in order to provide complete use of chlorine.

Reaction units employed for carrying out these processes are of three types (Fig. 2.10). In the first variant, the reaction is carried



Types of reactors for ionic-catalytic chlorination in the liquid phase: *a*—with external cooler; *b*—with heat removal by evaporation; *c*—chlorination combined with fractionation.

bubbling column (Fig. 2.10a) with external cooling and condenser, in which the entrained product vapours are condensed in the off-gas. The condensate is returned to the reactor and purified product is withdrawn through the side discharge sent for further refining. When acetylene is chlorinated, reactants being fed as indicated above there are observed the column, which is why the chlorine is introduced into the circulation circuit after its solution in tetrachloroethane is prepared. A chlorine solution then reacts with the bubbling acetylene. The relatively volatile, 1,2-dichloroethane is to be produced, and a considerable amount of heat evolved is removed by the reflux condenser. Moreover, the external cooler may be omitted, in which case the heat is removed by evaporation. A further improvement of the process is the omission of the side discharge pipe and the removal of the product duct from the system after the reflux condenser, when the condensate is returned to the column to maintain the temperature and the liquid level (Fig. 2.10b). In this case, the system does not contaminate the product and operates in the

column for a long time, being consumed little per unit amount of the product.

Finally, systems with combined chlorination and fractional distillation are now employed (Fig. 2.10c). Ethylene and chlorine are fed into the still, which operates as the reactor. In the fractionating section of the column, dichloroethane is separated from trichloroethane collected in the still and from the light distillate and the off-gas, the heat of reaction being used efficiently for the separation of the products.

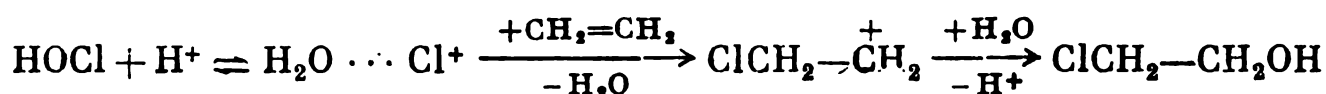
The off-gas is treated in the same way as for liquid-phase radical-chain chlorination, the only difference being that, because of the small amount of HCl, it is usually absorbed by water, the diluted hydrochloric acid being discharged into the sewer system. In order to reduce the amount of waste waters, it is, however, better to produce more concentrated acid and use it for plant needs. The liquid reaction products are purified, if necessary, from the catalyst and subjected to fractional distillation.

2.3.1.2. The Chlorohydration Reaction

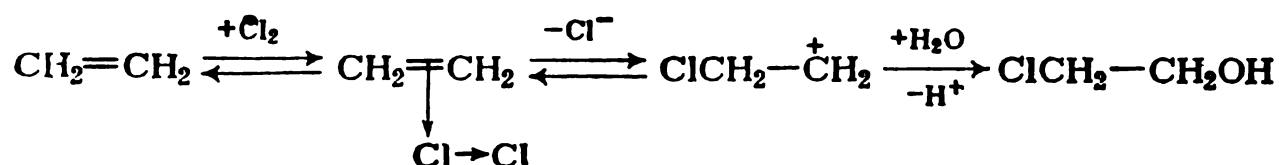
In contrast to the above described addition of chlorine across the double bond in aprotic solvents, the action of chlorine on olefins in an aqueous medium yields chlorohydrins:



It was formerly believed that the chlorohydration proceeds by way of addition of hypochlorous acid, which results from the hydrolysis of chlorine with water ($\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HClO} + \text{HCl}$), which is why the reaction was named hypochlorination. It was later found that hypochlorous acid in a neutral medium reacts with olefins very slowly and that the process is strongly accelerated with increasing acidity of the solution. This is accounted for by the formation of the hydrated chloride cation, which is a strong electrophilic agent capable of adding on an olefin across the double bond to form a σ -complex; the subsequent interaction with water gives chlorohydrin:



When the reaction is carried out with an aqueous solution of chlorine, the formation of the chloride cation is hardly probable. It is believed that in this case the electrophilic agent that attacks the double bond is the chlorine molecule:



is confirmed by the fact that the reaction rate is described by simple second-order equation:

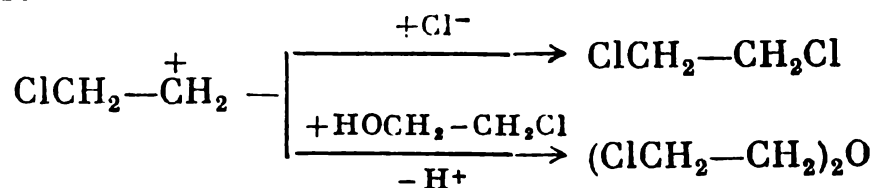
$$r = k[\text{RCH}=\text{CH}_2][\text{Cl}_2]$$

The reactivity of olefins varies in the same increasing order as chlorine additions:



Thus, for the homologues of ethylene and their derivatives the chlorohydrin formation proceeds in such a manner that chlorine (like a proton in the addition of acids to olefins) links itself preferably to the more oxygenated carbon atom. This results in the formation of 1-chloropropanol, $\text{ClCH}_2-\text{CH}(\text{OH})-\text{CH}_3$, with an impurity of isomeric chloro-1-propanol, $\text{HOCH}_2-\text{CHCl}-\text{CH}_3$.

The interaction of the intermediate σ -complex with the chloride ion accumulated during the reaction (from HCl) and chlorohydrin leads to the formation of two by-products—dichloride and dichloroalkyl ether:



These side reactions are consecutive with respect to chlorohydrin formation, which is why the selectivity strongly depends on the concentration of Cl^- anions and chlorohydrin in the aqueous solution attained. This dependence typical of all the chlorohydrination processes is shown in Fig. 2.11. It can be seen that a satisfactory yield of the major product is achieved only when dilute aqueous solutions of chlorohydrins are prepared. The selectivity also depends on the reactor used, which must be designed as close to the plug-flow model as possible.

Products Obtained by Chlorohydrin

The industrial significance of this process consists in the fact that chlorohydrins when treated with alkalis give the α -oxides of olefins:

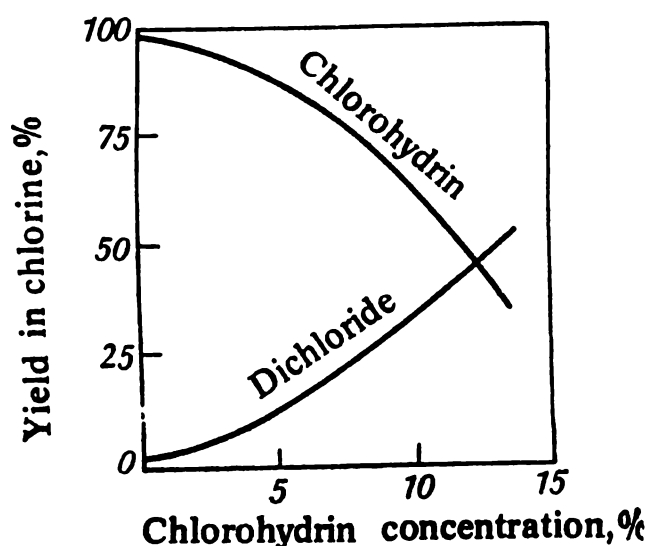
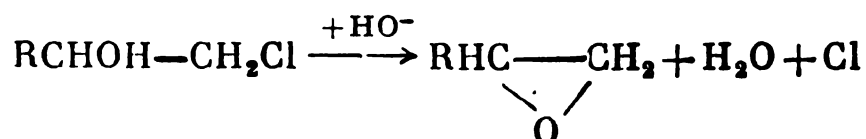
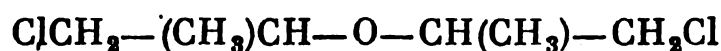


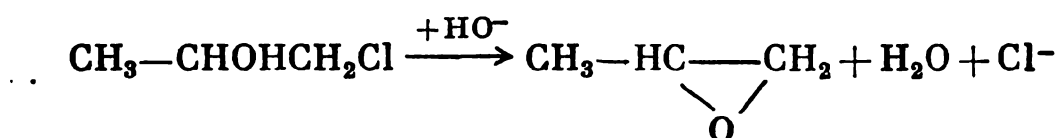
Fig. 2.11. Dependence of the yield of chlorohydrin and dichloride in the chlorohydrination of ethylene on the concentration of chlorohydrin in solution.

This route was formerly used to prepare ethylene oxide via *ethylene chlorohydrin*, $\text{HOCH}_2\text{—CH}_2\text{Cl}$, but today more economical routes have been found for the synthesis of this compound. The method still employed for the production of propylene chlorohydrin and glycerol dichlorohydrin.

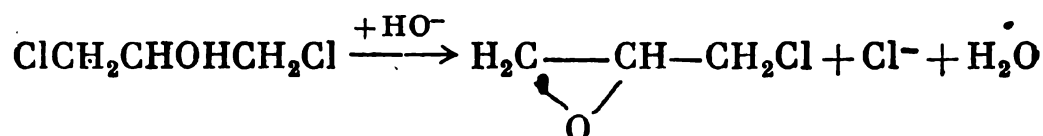
Propylene chlorohydrin, $\text{CH}_3\text{—CH(OH)—CH}_2\text{Cl}$, containing its isomer as an impurity, is prepared by chlorohydrination of propylene in the form of a 7-8-percent aqueous solution. The by-products formed are 1,2-dichloropropane and β,β' -dichlorodiisopropyl ether



Propylene chlorohydrin is used for the production of propylene oxide:



Glycerine dichlorohydrin, $\text{ClCH}_2\text{—CH(OH)—CH}_2\text{Cl}$, together with its isomer, $\text{HOCH}_2\text{—CHCl—CH}_2\text{Cl}$, is prepared by chlorohydrination of allyl chloride in the form of a 5-percent aqueous solution; the by-products formed are 1,2,3-trichloropropane and a mixture of tetrachloropropyl and isopropyl ethers, such as $(\text{ClCH}_2)_2\text{CH—O—CH(CH}_2\text{Cl})_2$. Both dichlorohydrins when treated with alkali give epichlorohydrin:



which is used for the manufacture of epoxy polymers, glycidyl ether and glycerol.

Process Technology. There are two methods of chlorohydrination. In the first method (Fig. 2.12a), propylene and chlorine are bubbled through an aqueous solution of the products in a hollow column protected against corrosion by ceramic plates. Water is also introduced into the lower part of the column; the heat evolved is removed by heating the water. If the gases contain inert impurities, part of the heat is removed by evaporation with the aid of a reflux condenser. Dichloropropane is also vaporized together with water. In order to separate the vapours, the condensate is sent to the separator. The water is returned to the column and the dichloropropane is withdrawn as a commercial product after purification. The chlorohydrin solution is decanted through the side overflow pipe; it is neutralized with lime and passed to the synthesis of propylene α -oxide.

The same method is employed for the production of glycerol dichlorohydrin, but allyl chloride is introduced as vapours diluted with a gas-carrier. Allyl chloride and chlorine dissolve well in the organic

phase (by-products); in which the addition of chlorine will take place; therefore, an increased dispersion of the mixture is important for increasing the selectivity. In the synthesis of dichlorohydrin, use is made of another method for carrying out the reaction, which consists of the preliminary preparation of a solution of hypochlorous

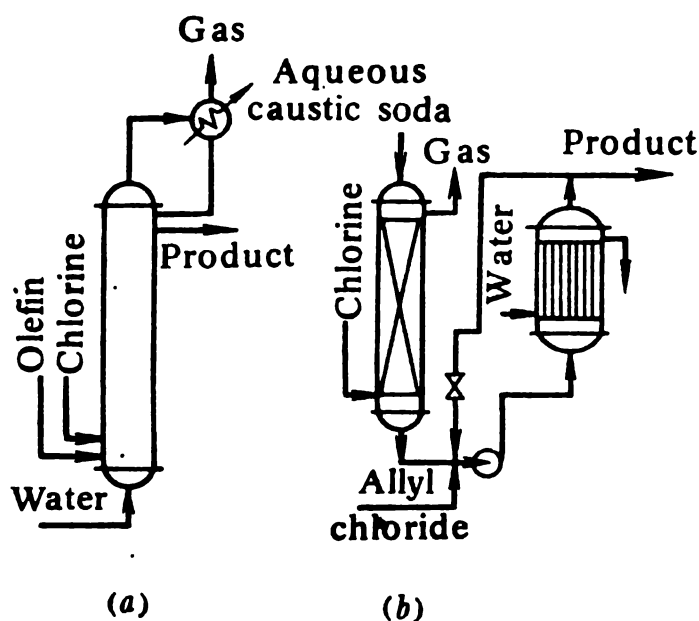
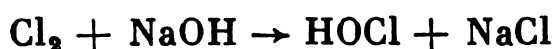


Fig. 2.12. Types of reaction units for chlorohydrination: *a*—bubbler column with a reflux condenser; *b*—reaction unit with separate production of hypochlorite and chlorohydrination in a tubular furnace with recycling.

acid (pH 5) and subsequent chlorohydrination. The solution indicated is prepared by passing chlorine through an aqueous solution of caustic soda or of sodium and calcium hydroxides:



The solution is then mixed with allyl chloride (in the pump) and pumped through the tubular reactor (which is cooled), part of the mixture being recycled (Fig. 2.12*b*). The yield of the chlorohydrins is 80-85 percent.

2.3.2. Hydrohalogenation Processes

Of these processes, only hydrohalogenation across double and triple carbon-carbon bonds is of great practical value.

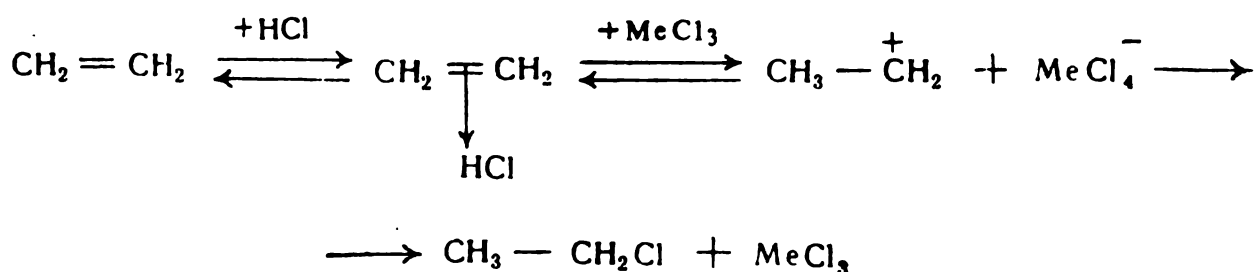
2.3.2.1. Hydrohalogenation at Double Carbon-Carbon Bonds

As was pointed out at the beginning of this chapter, hydrohalogenation is an exothermic reversible reaction:



Its equilibrium is shifted to the right with decreasing temperature and at temperatures lower than 50 °C the reaction becomes practically irreversible.

The reactivity of various hydrogen halides increases in the sequence which is the inverse of the order of the reactivity of free halogens ($\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$). The compounds HI and HBr not infrequently add on without catalysts, but the presence of catalysts is necessary for hydrochlorination. The catalysts used are aprotic acids, most frequently AlCl_3 or FeCl_3 . The reaction mechanism is electrophilic, the activating effect of MeCl_3 being accounted for by the fact that the steps of conversion of the π -complex to the σ -complex is facilitated:



or by the intermediate formation of the metal hydrochloric acid HAlCl_4 (or HFeCl_4), in which the proton becomes very active. The two mechanisms may be described by the same kinetic equation, which has been derived experimentally:

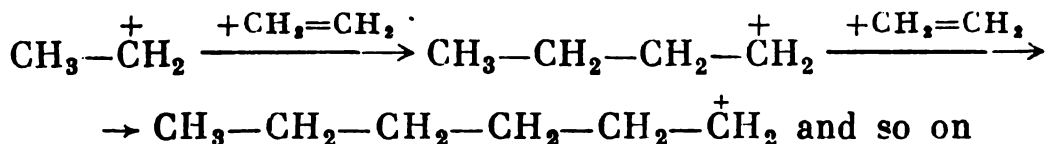
$$r = [\text{MeCl}_3][\text{HCl}][\text{RCH}=\text{CH}_2]$$

These mechanisms determine the same order of the reactivity of unsaturated compounds as in halogen addition reactions:



and also the direction of the addition reaction according to the Markovnikov rule, i.e., the hydrogen links itself to the most hydrogenated carbon atom and chlorine adds on to the less hydrogenated carbon atom.

The hydrochlorination process is usually accompanied by the side reaction of polymerization of unsaturated compounds, which is also catalyzed by MeCl_3 :



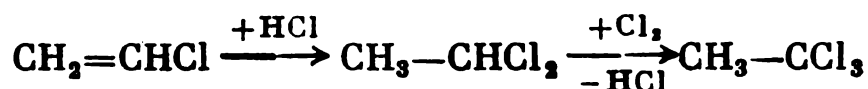
This gives liquid low-molecular polymers, the yield of which increases with increasing temperature (Fig. 2.13). The polymer yield is lowered by a relatively low temperature and an excess of HCl, which provides also the more complete conversion of the organic reagent.

Products Obtained by Hydrohalogenation. The most valuable of these is *ethyl chloride*, $\text{C}_2\text{H}_5\text{Cl}$, which is a gas under normal conditions (b.p. $+12.3^\circ\text{C}$). It is manufactured by the addition of hydro-

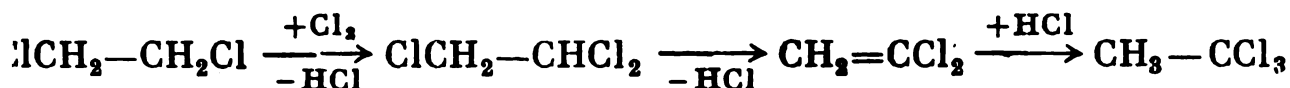
c acid to ethylene in the presence of a catalyst such as aluminium chloride (AlCl_3); lower polymers are formed as by-products. Ethyl chloride is extensively employed as an ethylating agent in the production of diethyldichlorosilane, $(\text{C}_2\text{H}_5)_2\text{SiCl}_2$, tetraethyl lead, $\text{Pb}(\text{C}_2\text{H}_5)_4$, ethyl mercaptan, $\text{C}_2\text{H}_5\text{SH}$, and ethyl-cellulose, and as a local anesthetic in medicine.

An analogous method is employed to produce *ethyl bromide*, $\text{C}_2\text{H}_5\text{Br}$, from ethylene and hydrogen bromide. Ethyl bromide is a colorless liquid (b.p. 38.4°C), which is used for the preparation of a compound known as tetraethyl lead; this compound is used as a gasoline knock additive (it raises its octane number).

Other hydrochlorination processes are associated with the production of a valuable solvent—*methylchloroform*, which has been described earlier. One of the methods of its preparation is based on ethylene chloride as the feedstock. Vinyl chloride is hydrochlorinated to ethyldichloride, $\text{CH}_3\text{—CHCl}_2$ (it is a liquid, b.p. 57.3°C), which is chlorinated by a radical-chain mechanism to methylchloroform:



In another method, the feedstock is 1,2-dichloroethane; the reaction involves the intermediate formation of 1,1,2-trichloroethane and ethyldichloride, and the hydrochlorination of the latter to methylchloroform:



The two processes may be combined using 1,1,2-trichloroethane, which is formed as a by-product in the chlorination of ethyldichloride, for the production of methylchloroform.

Process Technology. In order to shift the equilibrium to the desired side and suppress the side polymerization reactions, the hydrochlorination is carried out at low or moderate temperatures (from -50 to $30\text{--}40^\circ\text{C}$); the excess of HCl is 3–5 percent. The hydrochlorination of ethylene and vinyl chloride is accomplished using the most convenient method of the interaction of the two gases—their bubbling

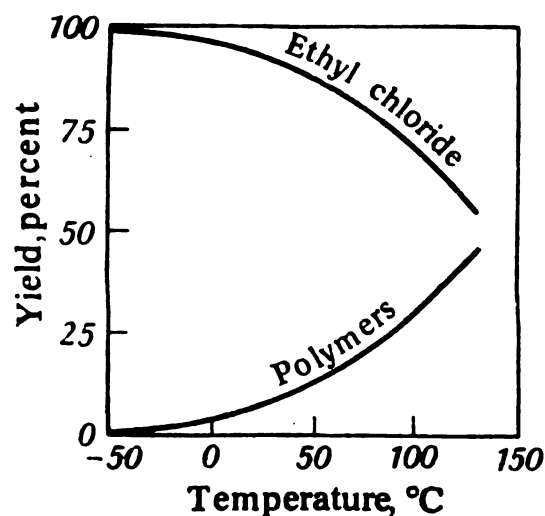


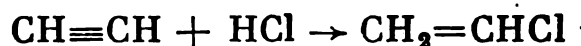
Fig. 2.13. Temperature dependence of the yield of ethyl chloride and ethylene polymers for the chlorohydration of ethylene in the presence of aluminium chloride.

ing through the liquid reaction product (just as in the case of the interaction of olefins with chlorine). The gases are dissolved in the liquid containing a catalyst and react in this solution. Here, the synthesis of ethyl chloride at a low temperature or elevated pressure is required in order to maintain ethyl chloride in the liquid state. When vinylidene chloride is subjected to hydrochlorination (this compound is a low-boiling liquid), it is bubbled through the solution.

The process is carried out in reactors of the type of bubble column, the design of the reaction unit being analogous to the one shown in Fig. 2.10a. The condensate is separated from the off-gas after the cooler and the excess hydrogen chloride is sent to water absorption. The liquid product that runs through the side overflow pipe of the column is neutralized with alkali and distilled. In the synthesis of ethyl chloride, apart from the scheme described, another scheme is also possible (Fig. 2.10b), in which the heat evolved is removed only by the reflux condenser due to the evaporation of the product in the reactor. Because of the high volatility of ethyl chloride, it must be extracted from the off-gas (by absorption or adsorption).

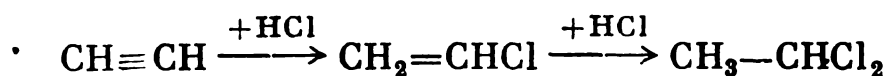
2.3.2.2. Hydrochlorination of Acetylene Hydrocarbons

The reaction of addition of hydrogen chloride to acetylene hydrocarbons is typical for compounds containing a triple bond:



The exothermicity of this reaction is two times stronger than that of the hydrochlorination of olefins ($-\Delta H_{298}^\circ = 112.4 \text{ kJ/mol}$ or 26.9 kcal/mol). Like the hydrochlorination of olefins, it is reversible to a certain extent, but at moderate temperatures its equilibrium is shifted almost completely to the right. For example, the equilibrium constants for the formation of vinyl chloride are equal to 8×10^3 at 200°C and 7×10^2 at 300°C .

The addition of HCl to acetylene proceeds consecutively with the formation of vinyl chloride and ethylene dichloride:

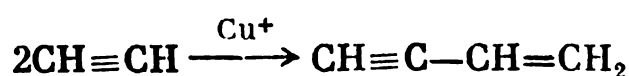


Therefore, the hydrochlorination of acetylene and its homologs is conducted in the presence of selective catalysts that speed up only the first addition step. Mercuric and cuprous salts have proved efficient for this purpose; an example is mercuric chloride, HgCl_2 , which strongly accelerates not only the main reaction but also the hydration of acetylene with formation of acetaldehyde. For this reason and also because of the deactivation of mercuric chloride in hydrochloric acid solutions it is used in the gas-phase process at $150\text{--}200^\circ\text{C}$, in which case the reagents as dry as possible are used.

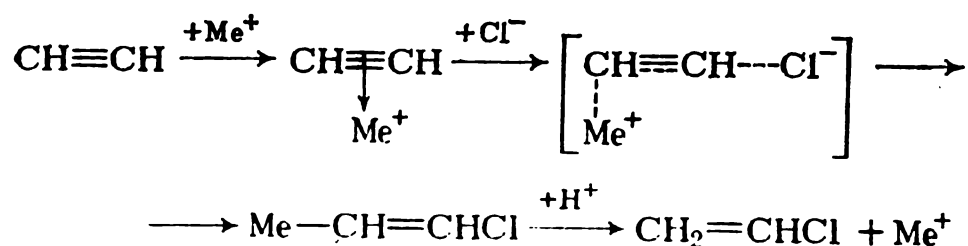
the process gives by-product acetaldehyde (due to a small moisture content) and ethylidene dichloride, but the yield of the latter does not exceed 1 percent.

The liquid-phase hydrochlorination process is effected using a cuprous salt, since it is not inactivated and has a weak accelerating effect on the interaction of acetylenic compounds with water. The catalyst is a solution of Cu_2Cl_2 in hydrochloric acid containing ammonium chloride.

In the presence of cuprous monochloride there occurs the side reaction of acetylene dimerization leading to vinyl acetylene:



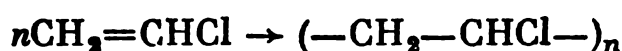
In order to suppress this side reaction, which occurs concurrently with the synthesis of a chloro derivative, a high concentration of hydrogen chloride is required and the catalyst must therefore be dissolved in concentrated hydrochloric acid. In the course of the process the acid is continuously "strengthened" by supplying hydrochloride to compensate for its consumption for hydrochlorination. The catalytic action of mercuric and cuprous salts on the hydrochlorination reaction is accounted for by the formation of coordination complexes, in which acetylene is activated and reacts with chloride anions, this leading to the intermediate formation of transition states with a metal-carbon bond or true organometallic compounds, which are rapidly decomposed by the acid:



Because of the simultaneous formation of less active or inactive complexes with HCl (or with chloride anions), the formation of vinyl chloride in the gas phase is described by the following kinetic equation:

$$r = k \frac{P_{\text{C}_2\text{H}_2} P_{\text{HCl}}}{1 + bP_{\text{HCl}}}$$

Products Obtained by Hydrochlorination of Acetylenic Hydrocarbons. *Vinyl chloride*, $\text{CH}_2=\text{CHCl}$ (a colourless gas, b.p. -13.9°C) has already been described. It is one of the most important monomers used extensively for the production of various polymeric materials. The polymerization of vinyl chloride in the presence of peroxides gives polyvinyl chloride:



It is also an intermediate in the synthesis of 1,1,2-trichloroethane, vinylidene chloride, and methylchloroform.

Chloroprene (chlorobutadiene), $\text{CH}_2=\text{CCl}-\text{CH}=\text{CH}_2$ (a liquid, b.p. 59.4°C) is produced industrially by the liquid-phase hydrochlorination of vinyl acetylene at $40-60^\circ\text{C}$ in the presence of cuprous monochloride:



Chloroprene is a valuable monomer used for the production of a synthetic rubber noted for high oil resistance.

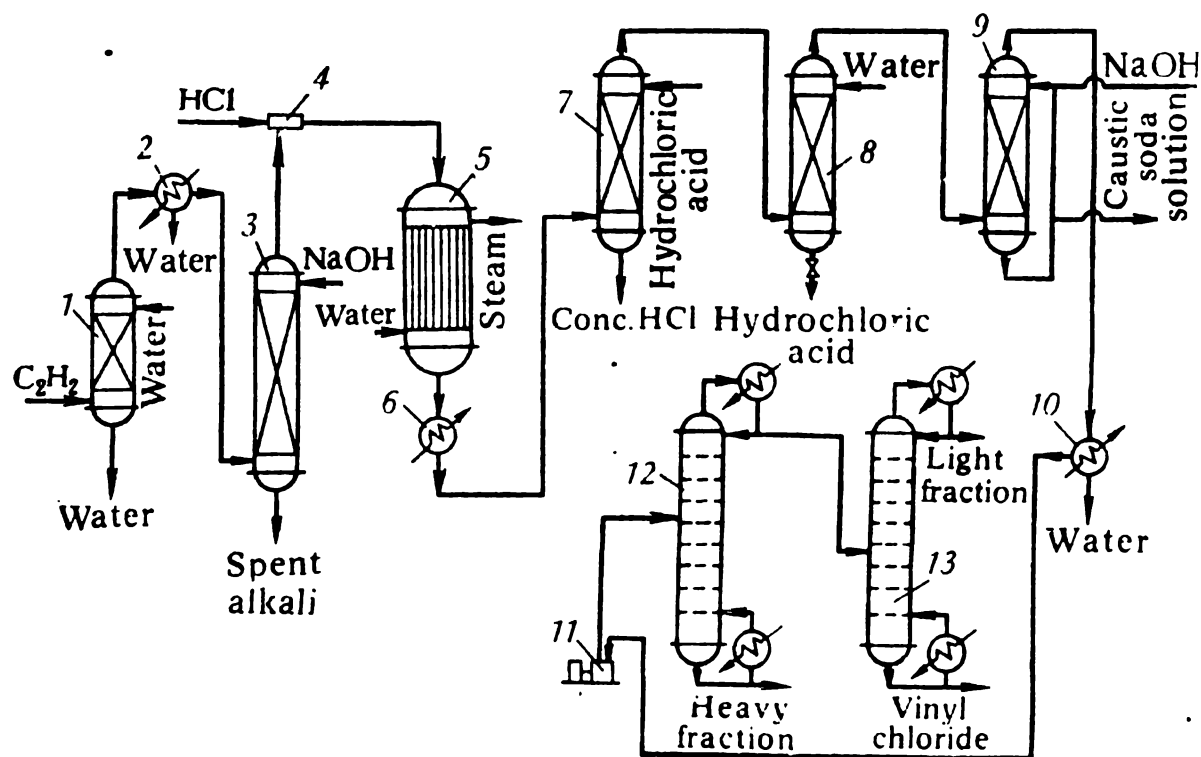
Production of Vinyl Chloride from Acetylene. The industrial synthesis of vinyl chloride from acetylene and hydrogen chloride is a gas phase heterocatalytic process. The catalyst is prepared by impregnating activated carbon with an aqueous solution of mercuric chloride with subsequent drying. The resulting catalyst contains 10 percent (by weight) of HgCl_2 . Because of the high toxicity of mercuric chloride and high inflammability of acetylene, strict safety and labour protection requirements are set up.

A mixture of acetylene and hydrogen chloride is passed through the reaction space filled with the solid catalyst. The reactants must be dry in order to prevent the excessive formation of acetaldehyde and corrosion of the apparatus. Hydrogen chloride is used in slight excess with respect to acetylene (5-10 percent), which increases the degree of conversion of acetylene. The optimal temperature is considered to be equal to $160-180^\circ\text{C}$, when the process occurs sufficiently rapidly and at the same time no excessive vaporization of mercuric chloride (which is highly volatile) takes place. With gradual loss of mercuric chloride and decrease of the activity of the catalyst the temperature is raised to $200-220^\circ\text{C}$.

Because of the strong exothermicity the process is carried out in tubular units: the tubes contain the catalyst and the gas mixture is flowing in them, and the refrigerant is circulating in the intertubular space. The refrigerants that may be used are organic compounds, water or water condensate; the water condensate boils under a certain pressure, which makes it possible to utilize the heat of reaction for steam generation.

The flow diagram of the production of vinyl chloride is shown in Fig. 2.14. The purified acetylene is passed through fire interrupter and dried first by the condensation of the moisture in brine cooler, and then by solid caustic in column 3. In mixer 4 it is mixed with dry hydrogen chloride and is led to tubular reactor 5. The degree of acetylene conversion is 97-98 percent, the reaction gases containing 93 percent of vinyl chloride, 5 percent of HCl , 0.5-1 percent of C_2H_4 and 0.3 percent each of acetaldehyde and 1,1-dichloroethane. They entrain vapours of mercuric chloride. The gas is chilled in cooler 6 and purified from mercuric chloride and HCl successively in scrub

7, 8, and 9 with 20-percent hydrochloric acid, water and circulating caustic. The gas is then dried in brine cooler 10 and compressed in compressor 11 to 0.7-0.8 MPa. The mixture is successively rated in fractionating columns 12 and 13; first the heavy residue (vinylidene dichloride) is separated and then the light distillate (ethylene, residual acetaldehyde).



2.14. Flow diagram of vinyl chloride production by chlorohydration of acetylene:

Legend: 2, 6, 10—coolers; 3—drying column; 4—mixer; 5—reactor; 7, 8, 9—scrubbers; 11—compressor; 12, 13—fractionating columns.

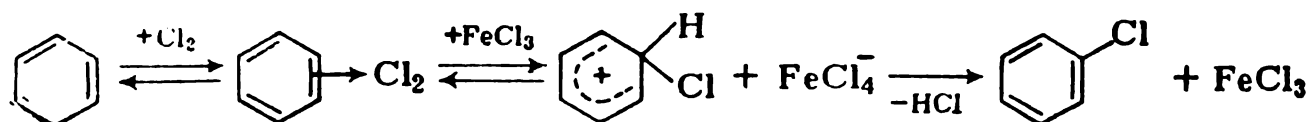
The methods of synthesis described above are not promising both for vinyl chloride and for chloroprene, though the existing plants are still operating. This is because acetylene is expensive and also because the use of highly toxic mercuric chloride is used in the production of vinyl chloride and in the synthesis of chloroprene the yield of the product is low. Other methods of production of these compounds will be described at a later time.

2.4. Nuclear Chlorination of Aromatic Compounds

We have already described the radical-chain chlorination of aromatic compounds (side-chain chlorination and chlorination in which chlorine adds on to the carbon-carbon bonds of the benzene ring). Nuclear substitution occurs in the presence of catalysts of these reactions when it becomes practically the only direction of chlorination of aromatic compounds.

Just as with the addition of chlorine and HCl to olefins, the catalysts for nuclear chlorination reactions are aprotic acids, of which

the cheapest FeCl_3 has assumed practical importance. Use is also made of iron, which generates FeCl_3 during the reaction. In contrast to the high-temperature radical-chain chlorination reaction, nucleophilic chlorination in the presence of catalysts proceeds by an electrophilic mechanism and through the formation of π - and σ -complexes

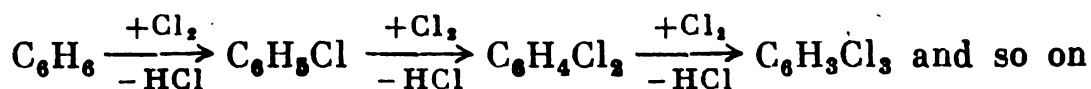


Another explanation is that there is preliminarily formed the complex $\text{Cl} \rightarrow \text{ClFeCl}_3$, in which one of the chlorine atoms becomes strongly electrophilic. The two mechanisms give the same rate equation which has been confirmed experimentally:

$$r = k[\text{FeCl}_3][\text{ArH}][\text{Cl}_2]$$

In accordance with this, the effect of the substituents in the benzene ring is different. The electron-donating groups (CH_3- , $\text{HO}-$) activate the nucleus and direct the substitution preferably into the *ortho* and *para* positions. The electron-withdrawing groups ($-\text{NO}_2$) deactivate the nucleus and orient the substitution preferably into the *meta* position. Finally, the halogen atoms, while deactivating the nucleus, direct the next chlorine atom mostly into the *ortho* and *para* positions. The chlorination is highly sensitive to the effect of substituents. For example, toluene is chlorinated many times faster than benzene, and phenol enters into the reaction even in the absence of catalysts.

Like other substitutive chlorinations, the process occurs according to the scheme of consecutive-parallel conversions:



with the successive replacement of the hydrogen atoms present until the exhaustive chlorination product is obtained. In this system reactions, because of the deactivating effect of chlorine each succeeding step proceeds more slowly than the preceding one, the difference in their rates being larger than in the chlorination of paraffins (for instance, chlorobenzene is chlorinated 8 times more slowly than benzene). Therefore, the product composition curves, which are in general similar to those given in Fig. 2.3, have higher maxima for the formation of intermediates, say 70-75 percent for chlorobenzene. The selectivity of the process is controlled, just as in other substitutive chlorinations, by changing the ratio of chlorine to the aromatic compound, but the excess of the latter is not large in the production of monochlorides, amounting to only a doubled or triple figure. It can be further reduced if the by-products are used for sp

lized purposes. In the production of polychlorinated compounds, is the excess chlorine that is used.

Products Obtained by Nuclear Chlorination. *Chlorobenzene*, $\text{C}_6\text{H}_5\text{Cl}$ (a liquid, b.p. 132°C) is produced by the chlorination of benzene with the formation of dichlorobenzenes as by-products. Chlorobenzene is used as a solvent and an intermediate for the synthesis of some nitrochlorobenzenes, chloroanilines, and nitrophenols. Formerly, chlorobenzene was the feedstock for the manufacture of phenol and the well-known insecticide DDT.

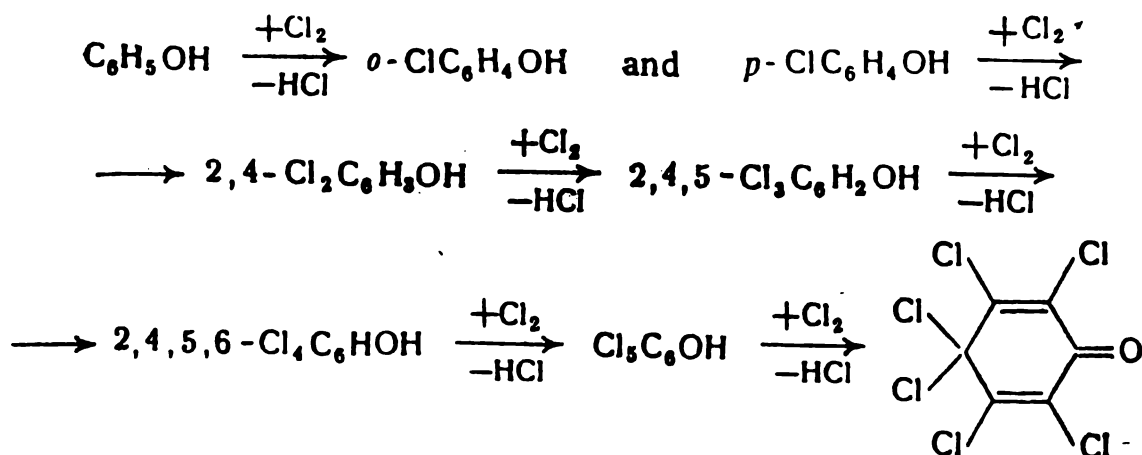
Dichlorobenzenes, $\text{C}_6\text{H}_4\text{Cl}_2$, which are formed as by-products in the manufacture of chlorobenzene, is a mixture of 40 percent of the *ortho*-isomer, 55 percent of the *para*-isomer, and 5 percent of the *meta*-isomer. *p*-Dichlorobenzene (m.p. 53°C) separated from this mixture by crystallization is sold as an insecticide. The remainder is technical *o*-dichlorobenzene which is used as a solvent.

Hexachlorobenzene, C_6Cl_6 (m.p. 231°C) is obtained by the chlorination of any benzene chloride. It is a fungicide and an intermediate in the synthesis of pentachlorophenol and the corresponding phenols.

Chloronaphthalenes, namely monochloronaphthalene ($\text{C}_{10}\text{H}_7\text{Cl}$) and a mixture of tri- and tetrachloronaphthalenes, are manufactured by the chlorination of naphthalene and used, respectively, for the preparation of tetraethyl lead solutions and a wax substitute (known as alowax).

Sovol is a chlorinated diphenyl with 4 or 5 chlorine atoms in the molecule. It is produced by the chlorination of diphenyl and used rather extensively as a plasticizer for polymers, an electric insulating and a lubricating oil, and as a wood preservative.

The chlorination of phenol gives successively the following chlorophenols:

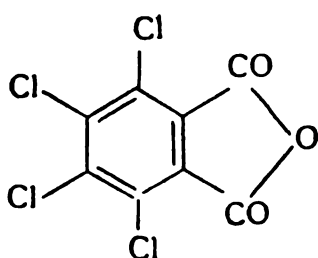


The last compound when subjected to hydrolysis gives tetrachloro-*p*-benzoquinone (*chloranil*), which is produced by the chlorination of pentachlorophenols in a sulphuric-acid medium and used in polymeric compositions.

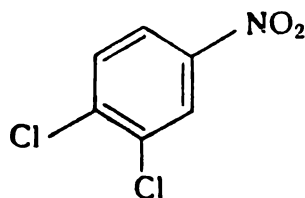
Pentachlorophenol is obtained by the chlorination of trichlorophenols or by the alkaline hydrolysis of hexachlorobenzene and used as an industrial antiseptic, especially for the preservation of wood. *Sodium pentachlorophenate*, C_6Cl_5ONa , is also used for the same purpose and also as a herbicide.

2,4-Dichlorophenol and *2,4,5-trichlorophenol* are manufactured by the chlorination of phenol. They are intermediates for the synthesis of valuable herbicides—the products of their condensation with the salt of monochloroacetic acid (2,4-D and 2,4,5-T preparations) which have the general formula $ArOCH_2COONa$. *2-Methyl-4-chlorophenol* produced by the chlorination of *o*-cresol is used for the same purpose.

Of other products of the chlorination of aromatic hydrocarbons, mention should be made of *tetrachlorophthalic anhydride* and *3,4-dichloronitrobenzene*:



Tetrachlorophthalic
anhydride



3,4-Dichloronitrobenzene

Tetrachlorophthalic anhydride is produced from phthalic anhydride and used for the preparation of noncombustible polymeric materials. 3,4-Dichloronitrobenzene, which is synthesized by the chlorination of *p*-chloronitrobenzene, is an intermediate for the synthesis of the herbicides propanil and diuron.

Process Technology. The processes under consideration are always carried out in the liquid phase by bubbling chlorine through the reactant, in which the products being formed are gradually accumulated. Technologically, this process is similar in some respects to radical-chain chlorination in the liquid phase and ionic-catalytic chlorination of olefins. The features common with the first process are the consecutive nature of reactions, the reaction unit and the off-gas processing step; the features common with the second process are the use of electrolytic chlorine gas, catalysts in the form of steel bars (or rings) or $FeCl_3$ and the processing of the liquid reaction mass.

The preparation of the feedstock consists of the drying of chlorine gas with sulphuric acid and the drying of the organic reagent by an azeotropic agent or by other means.

The chlorination process is carried out as a batch or continuous process, the removal of a large amount of heat being very important.

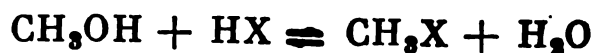
in both cases. It was formerly believed that the chlorination of benzene should be carried out at as low a temperature as possible and the heat was removed by cooling the reaction mass with water, which limited the capacity of the reaction unit. It was later found that the temperature has no substantial effect on the composition of the products and the process was conducted at 70-100 °C, the heat being removed in a more efficient way—by the evaporation of excess benzene with the aid of a reflux condenser. The same method is employed for the chlorination of higher-boiling compounds when the process is carried out in a solution of a low-boiling solvent (say, in a solution of 1,2-dichloroethane). In such cases, the reaction unit is similar to the one shown in Fig. 2.5c; in order to suppress the side reactions of more complete chlorination the column should be fitted with trays. The chlorination of some high-boiling compounds (phenol, naphthalene) is accomplished, however, in the liquid mass or in molten substances without using a solvent. The heat is removed with the aid of external or internal coolers, using reaction units similar to those shown in Fig. 2.5a and b for batch and continuous processes. When several chlorine atoms are introduced, in which case the reaction velocity falls and the melting point of the mixture increases, the reaction temperature is gradually raised up to 150-180 °C.

The processing of the off-gas consists in recovering the volatile organic chlorine substances (by cooling or absorption) and utilizing HCl with formation of concentrated hydrochloric acid. The design of the reaction unit is analogous to the one shown in Fig. 2.7. The processing of the liquid products consists of the neutralization of HCl and the catalyst by water and aqueous caustic, following which the products are separated by distillation or crystallization.

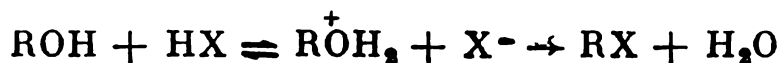
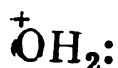
2.3.4. Halogenation of Oxygen-Containing and Nitrogen Compounds

2.3.4.1. Halogenation of Alcohols, Aldehydes and Ketones

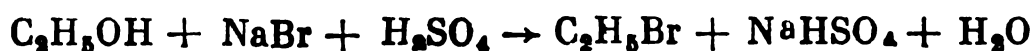
Hydrohalogenation of Alcohols. The reaction involves the replacement of the hydroxyl group by chlorine or bromine atoms; it is effected by the action of HCl (or HBr) on alcohols and is a reversible exothermic reaction:



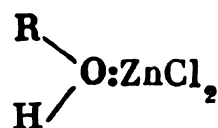
For tertiary, secondary and higher primary alcohols, the reaction may be carried out in the liquid phase in the absence of catalysts by shifting the equilibrium through the distillation of water or the chloro derivative. The reaction mechanism consists of the protonation of the alcohol and subsequent nucleophilic replacement of the group



In other cases, especially with lower primary alcohols, there are required catalysts, which sometimes play the role of water-removing agents, displacing the equilibrium to the right. For example, in order to obtain ethyl bromide, use is made of concentrated sulphuric acid, which simultaneously generates HBr from sodium bromide:



For liquid-phase processes use is sometimes made of a saturated solution of ZnCl_2 in hydrochloric acid, and for gas-phase reactions of ZnCl_2 on porous supports. The function of zinc chloride as an aprotic acid is to exert a direct activating effect on the alcohol molecule:



or to form the strong acid H_2ZnCl_4 , which protonates the alcohol.

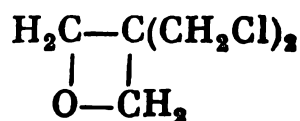
The largest multitonnage product manufactured by the hydrochlorination of alcohols is *methyl chloride*, CH_3Cl , which has been described earlier. It is produced from anhydrous HCl and methanol in the gas phase in the presence of a heterogeneous catalyst (ZnCl_2 or silica gel or on pumice) at 200–350 °C using a 20- to 50-percent excess of HCl to displace the equilibrium. The reaction is carried out in a tubular or adiabatic reactor with a fixed bed of a heterogeneous catalyst. The reaction products, which consists of the unconverted reagents, CH_3Cl , H_2O and by-product dimethyl ether, are cooled; as a result, hydrochloric acid and methanol are condensed from them. The methanol is distilled off and returned to the reaction. The gaseous mixture is purified from methanol and HCl by water and aqueous caustic. The methyl chloride is then freed from the dimethyl ether by concentrated sulphuric acid, neutralized, dried and condensed under pressure. For the synthesis of methyl chloride this method is most frequently employed and is more economical than the chlorination of methane.

Apart from *ethyl bromide* and also *methyl bromide*, CH_3Br , the hydrohalogenation of alcohols is sometimes used to produce certain higher alkyl chlorides and chlorohydrins of polyhydric alcohols. Especially interesting among the chlorohydrins are pentaerythritol di- and trichlorohydrins:

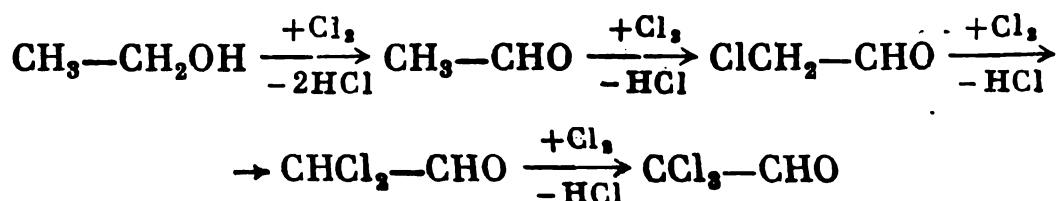


which are produced from anhydrous HCl and pentaerythritol in the presence of acetic acid. They are used for the production of the

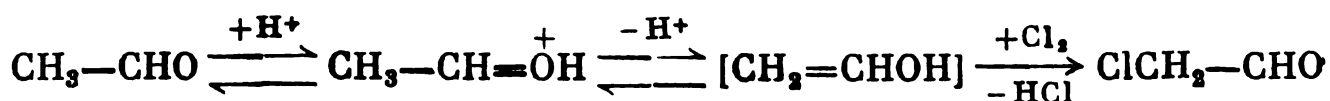
nonomer bis(chloromethyl)oxacyclobutane:



Chlorination of Alcohols, Aldehydes and Ketones by Free Chlorine. The initial reaction in the chlorination of alcohols by free chlorine involves the oxidation of an alcohol to an aldehyde or ketone followed by the sequential replacement of the hydrogen atoms in the alkyl group by chlorine:



If the reactant is an aldehyde or ketone, the reaction reduces to the replacement of the hydrogen atoms bound to the carbon atom adjacent to the carbonyl group. The rate of the chlorination of carbonyl compounds is proportional to their concentration, does not depend on the chlorine concentration and is speeded up by acids, in particular by the HCl formed. This led to the belief that the rate-limiting step is the enolization followed by the rapid interaction with chlorine:



Of the chlorination products of alcohols, aldehydes and ketones, *1,1,3-trichloroacetone* and *hexachloroacetone* are of little value, the most important product being *chloral*, CCl_3-CHO . This liquid (b.p. 97.8°C) is used for the manufacture of a number of valuable pesticides, notably sodium trichloroacetate and Trichlorfon (Dipterex).

Chloral is produced industrially by the chlorination of ethanol; the first two steps proceed at a high rate and the final step relatively slowly. It is because of this that in the batch process the temperature is raised from 40 to $80-90^\circ\text{C}$. In the continuous synthesis the process is conducted in a cascade of two bubble columns with the gas and liquid being in countercurrent contact with each other (Fig. 2.15). The alcohol and the mixture of chlorine and HCl after the second step are led to column 1, where a temperature of $55-65^\circ\text{C}$ is maintained by cooling. The liquid containing a mixture of chloroacetaldehydes, their acetals and semiacetals passes into the second column, which operates at 90°C and into which chlorine and water are introduced. The function of water is to hydrolyze the acetals, which provides the more complete use of the alcohol.

The product obtained after the second column is a mixture of chloral hydrate, chloral semiacetal and the corresponding derivatives of dichloroacetaldehyde. It is treated with concentrated sulphuric acid, the hydrates and acetals being broken down with formation of free chloral:



Chloral is settled down from sulphuric acid and subjected to distillation, the light fraction containing dichloroacetaldehyde being

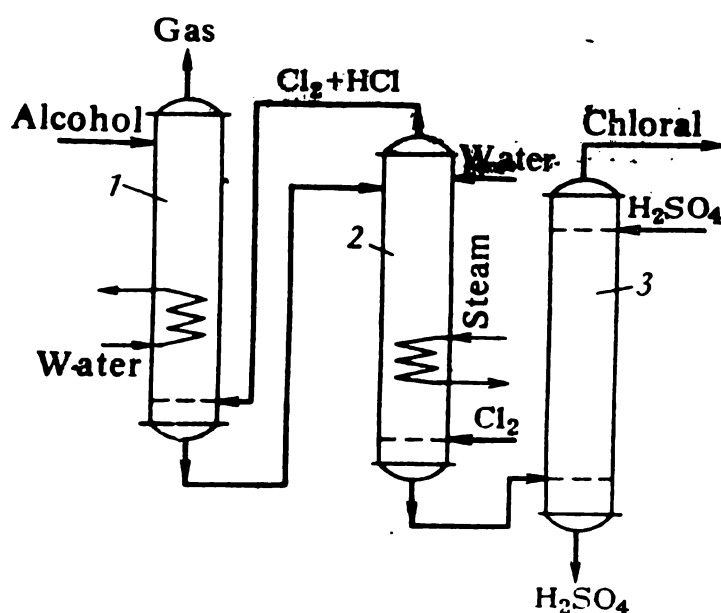
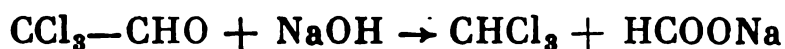


Fig. 2.15. Reaction unit for chloral production:
1, 2—reaction columns; 3—scrubbing column.

returned to the chlorination. The product obtained is 97-98 percent pure.

When acted on by alkalis chloral decomposes into chloroform and sodium formate:

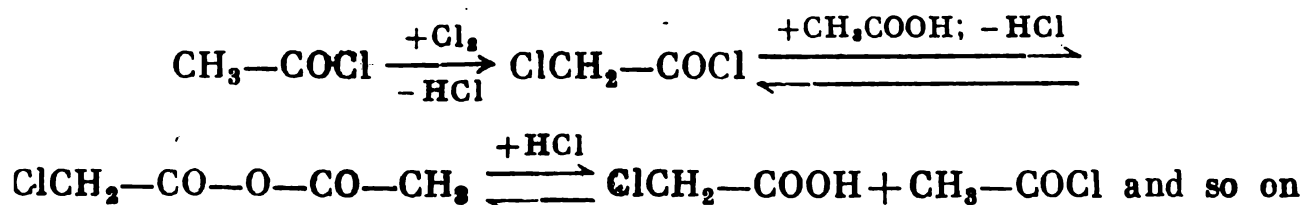


This reaction was formerly the basis of the method of preparing chloroform from ethanol and calcium hypochlorite, which is of no value at present.

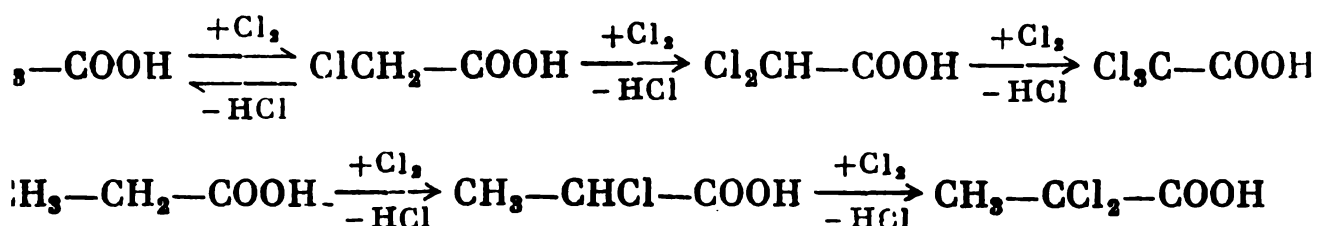
2.3.4.2. Chloro-Organic Synthesis of Acid Derivatives

Chlorocarboxylic acids of the aliphatic series are commonly produced by the chlorination of carboxylic acids. This reaction is catalyzed by substances (PCl_3 , sulphur chlorides) capable of forming with carboxylic acids anhydrides and acid chlorides, which are also catalysts. Their effect is accounted for by the fact that, in contrast to the acids themselves, acid chlorides interact sufficiently rapidly with chlorine and the formation and splitting of the anhydrides leads

chlorocarboxylic acids:



Reaction is accompanied by the consecutive formation of products upon substitution at the carbon atom linked to the carboxyl group:



Composition of the products is controlled, as usual, by varying the ratio of chlorine to the carboxylic acid, which is facilitated by the strong slowing-down of the subsequent chlorination steps. The reaction is carried out by bubbling chlorine gas through the liquid mass of the acid and catalyst with the temperature being gradually raised from 100 up to 150-170 °C.

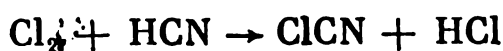
Monochloroacetic acid, $\text{ClCH}_2\text{—COOH}$ (a crystalline substance), prepared by the chlorination of glacial acetic acid with acetic anhydride as catalyst. It is marketed in the form of the free acid or sodium salt and used for the production of herbicides of the type of *o*-phenoxy acetates, $\text{ArOCH}_2\text{—COONa}$, and also of carboxymethyl cellulose, $\text{Cell—CH}_2\text{—COONa}$.

Trichloroacetic acid, $\text{Cl}_3\text{C—COOH}$, in the form of its sodium salt a valuable herbicide. Three chlorine atoms are difficult to introduce into the molecule of acetic acid, which is why trichloroacetic acid is produced on the technical scale by the oxidation of chloral with nitric acid:



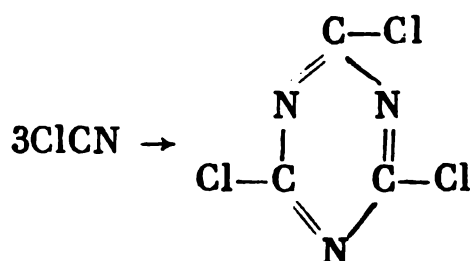
Dichloropropionic acid, $\text{CH}_3\text{—CCl}_2\text{—COOH}$, is prepared by the chlorination of propionic acid in the presence of PCl_3 and phenol as catalysts. In the form of its sodium salt it finds wide application as a herbicide.

Cyanogen chloride, ClCN (a gas with a pungent odour; b.p. 12.6 °C) is the acid chloride of cyanic acid (HOCN) and is hydrolyzed to its acid in an alkaline medium. In a neutral aqueous medium it is stable, and in the presence of acids it is polymerized. Cyanogen chloride is produced on the technical scale by the chlorination of hydrocyanic acid in an aqueous solution:



Cyanogen chloride is the most volatile component of the mixture; it is continually distilled off from the reaction mass, condensed and dried, since the water impurity causes its polymerization during storage.

Cyanogen chloride is used for the manufacture of cyanuric trichloride by cyclotrimerization in the presence of acid catalysts:

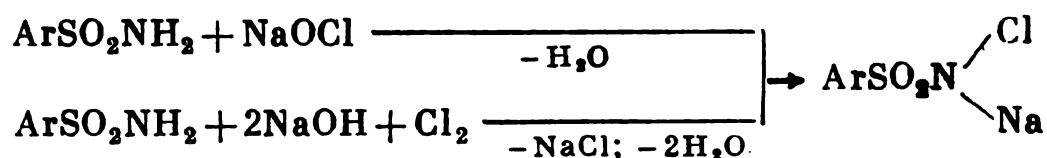


Cyanuric trichloride (a crystalline solid; m.p. 146 °C) is prepared by this reaction in the gas or liquid phase. In the first case, the process is carried out at 400 °C in tubular reactors with activated carbon as catalyst; for the liquid-phase reaction use is made of the catalysis with hydrochloric acid or ferric chloride at 300 °C and 4 MPa. Cyanuric trichloride is used chiefly for the synthesis of herbicides of the triazine series (simazine, propazine).

2.3.4.3. Chlorination at the Nitrogen Atom

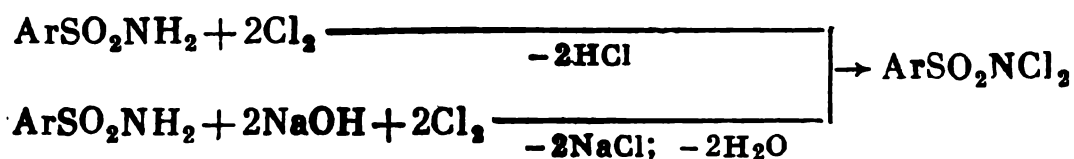
We have so far described only those reactions in which chlorine becomes linked to carbon atoms (C-chlorination). But there are conversions that lead to the formation of N—Cl bonds (N-chlorination). Such reactions are exhibited by acid amides; the chloramides obtained by their chlorination are called chloramines, which is not quite correct. They contain active chlorine atoms and have found wide application as mild disinfectants and bleaching agents. The most important of acid amides are chloramides of arylsulphonic acids.

Monochloramines B and *T* are the monosodium salts of monochloramides of benzene- or toluene-sulphonic acids. They are obtained by treating benzene or toluene sulphonamides with sodium hypochlorite or by the interaction of alkaline solutions of these sulphonamides with chlorine in an aqueous solution:



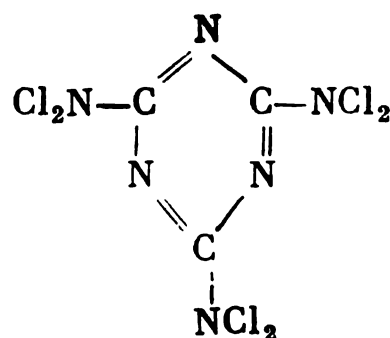
The monochloramines formed are crystallized and obtained in pure form. They are soluble in water and are used in the form of 0.5-5-per cent aqueous solutions.

Dichloramines B and *T* are the dichloramides of benzene- or toluene-sulphonic acids. They are produced by the chlorination of a water suspension of sulphamides or alkaline solutions of sulphamides:



Dichloramines are precipitated as crystals; they are then filtered off and dried. They do not dissolve in water and are used in the form of solutions in organic solvents.

Carbamide, $\text{CO}(\text{NH}_2)_2$, and melamine are also capable of N-chlorination. *Hexachloromelamine* obtained from melamine upon chlorination,



has a high content of active chlorine and is a strong disinfectant.

2.4. Decomposition Reactions of Chloro Derivatives.

Combined and Coupled Chlorination Reactions

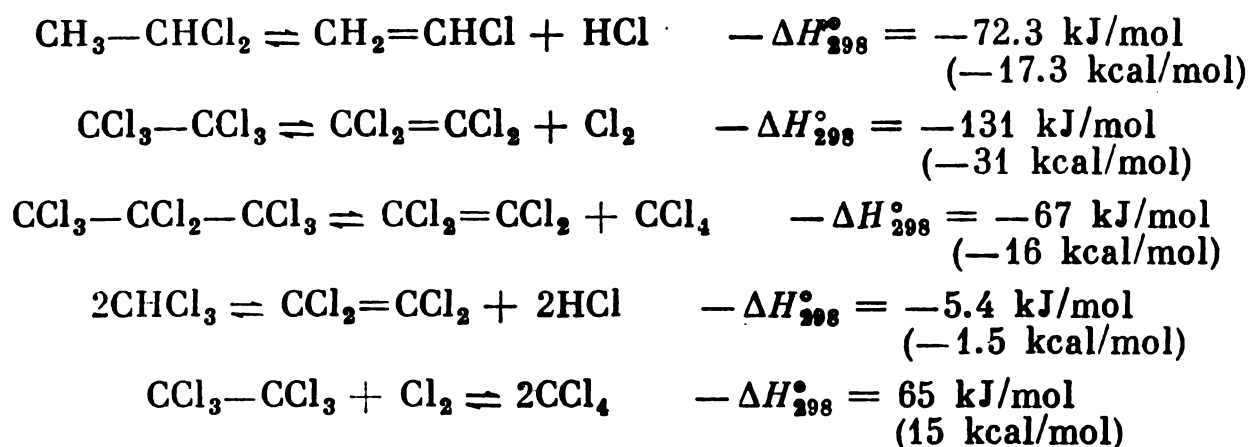
All the syntheses described above are classical in the chemistry and technology of chlorination processes and have long been known and employed on an industrial scale. Some of these processes, however, have a number of disadvantages, which is why new combined and coupled chlorination reactions have been developed, which are based on the reactions of thermal or thermocatalytic splitting of chloro derivatives and oxidative chlorination.

Their development has been invoked by the desire to lower the product cost, which can be achieved: (1) by replacement of chemical reagents (caustic) for the elimination of HCl by thermal dehydrochlorination; (2) by replacement of a more costly organic raw material, say acetylene, by ethylene and ethane; (3) by complete utilization of chlorine, half of which is released in the form of HCl in substitutive chlorinations; (4) by conversion of by-product polychlorides and other wastes into valuable chloro organic products,

which simultaneously solves the problem of environmental protection; (5) by reduction of the investment cost for combined and coupled reactions.

2.4.1. Decomposition Processes, Their Combination and Coupling with Chlorination Reactions

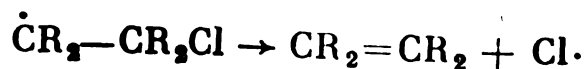
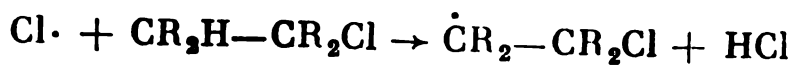
Thermodynamics, Mechanism and Kinetics of Decomposition Reactions. The most important decomposition reactions of chloro derivatives are the following typical classes of conversions:



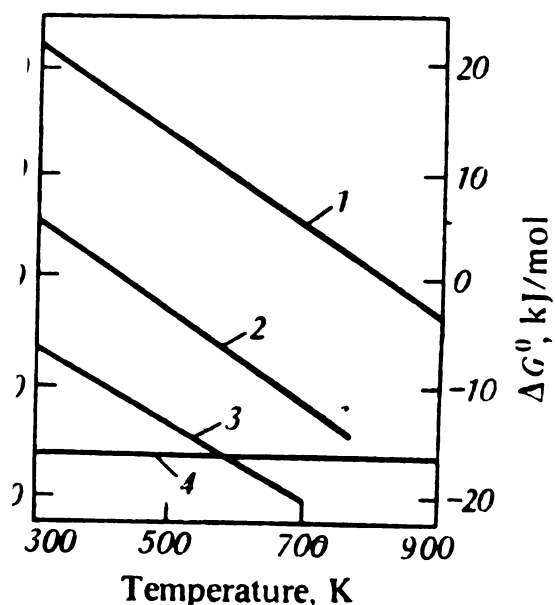
Most of these reactions are more or less endothermic; only the last chlorinolysis reaction proceeds with evolution of heat. The dependence of the Gibbs free energy for some dehydrochlorination reactions on temperature is shown in Fig. 2.16. It can be seen that the change of the sign of the free energy occurs for these reactions at about 500 K; above this temperature the elimination of HCl becomes dominant. The thermodynamic feasibility of this reaction increases with increasing carbon chain length and with chlorine being attached to the secondary and especially to the tertiary carbon atom and also, for polychlorides, with several chlorine atoms attached to the carbon atom. For other decomposition reactions the temperature dependence of the free energy is more complicated (Fig. 2.17). The dechlorination reaction begins to predominate over chlorine addition at about 800 K and the pyrolysis of perchloro derivatives across the carbon-carbon bond is possible even at 400-450 K, i.e., at a temperature much lower than that for hydrocarbons. By contrast, the condensation of polychlorides with elimination of HCl and the chlorinolysis reaction are thermodynamically feasible at all temperatures.

In spite of these thermodynamic relationships, all the reactions under consideration proceed at a sufficiently high rate only at a high temperature (400-600 °C) and by a radical-chain mechanism under these conditions. Chain initiation is effected by way of the rupture of the carbon-chlorine bond in the molecules of halogen derivatives, but in the presence of chlorine the chain initiation with the rupture of the weaker chlorine-chlorine bond is energetically

is favourable. Thus, chlorine is an initiator for these processes, which is often used to speed up these reactions and to lower reaction temperature. The chain propagation in dehydrochlorination reactions proceeds as follows:



In the absence of chlorine this reaction is first order in the chloro derivative ($r = kP_{\text{RCl}}$), and in the case of initiation by chlorine the



2.16. Temperature dependence of the free energy change for dehydrochlorination reactions:

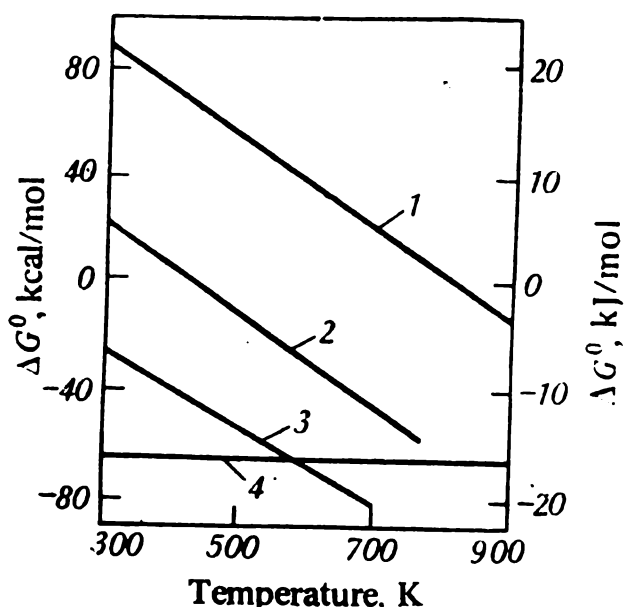
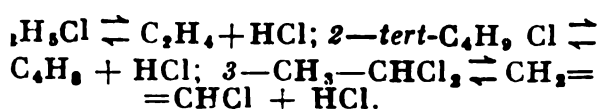
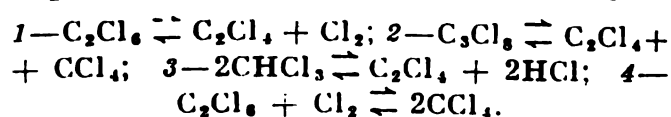
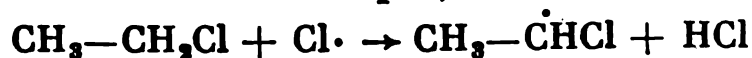


Fig. 2.17. Temperature dependence of the free energy change for the decomposition of chlorine derivatives:



reaction order is from 0.5 to 1 in the chloro derivative and 0.5 in chlorine ($r = kP_{\text{Cl}}^{0.5}P_{\text{RCl}}^{0.5-1}$), which corresponds to quadratic chain termination. The rate-limiting step for various chloro derivatives probably varies, depending on their structure.

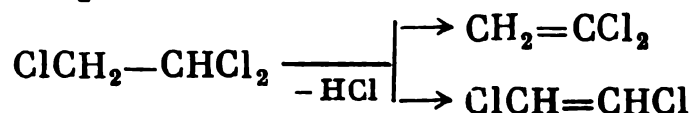
Some chloro derivatives are dehydrochlorinated thermally at a very slow rate and by a molecular mechanism. This refers to ethyl chloride, 1,1-dichloroethane and similar compounds formed upon lack of a chlorine atom on the free radicals, from which the chlorine cannot be eliminated for example,



Such compounds undergo elimination more readily by an ionic mechanism, which is feasible in the presence of catalysts of the type of protic acids (metal chlorides, pumice, silica gel).

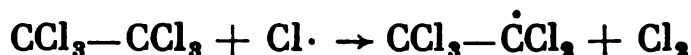
The direction of HCl elimination is determined by the Zaitsev rule, according to which the hydrogen atom which is eliminated comes

from the carbon atom carrying the smaller number of hydrogen atoms. For example, from 1,1,2-trichloroethane there is mainly obtained vinylidene chloride, but a considerable amount of 1,2-dichloroethane is also produced:

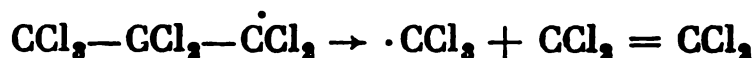
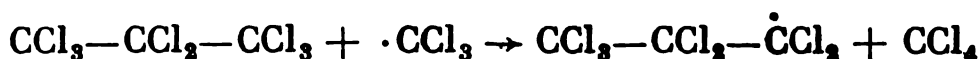


In this respect, the thermal elimination of HCl proceeds less selectively than under the action of alkalis.

The dechlorination reaction occurs by the following mechanism:

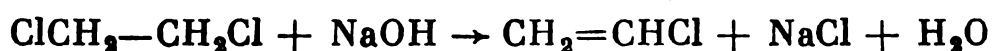


Upon cracking the chain is continued by the perchloroalkyl radicals

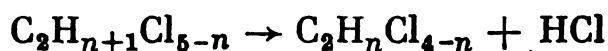


The mechanism of condensation and chlorinolysis reactions is more complicated. These reactions are also accelerated by heterogeneous catalysts (activated carbon, pumice), but their role has not yet been clarified.

Technology of Thermal Elimination of HCl Combined with Chlorination Reactions. The interest in thermal dehydrochlorination was invoked by the possibility of replacing the older method of HCl elimination with the aid of alkalis in the production of chloroolefins, say in the manufacture of vinyl chloride from 1,2-dichloroethane:



This method is still exploited for the production of vinylidene chloride and tri- and tetrachloroethylenes, but it has a number of disadvantages: the consumption of alkali, the loss of chlorine (in the form of a salt), the formation of a considerable amount of waste water. Thermal dehydrochlorination has eliminated all these shortcomings and enabled the more economical production of chloroolefins:



This reaction is used to produce vinyl chloride, as has been said earlier, and also the following olefin chlorides.

Vinylidene chloride, $\text{CH}_2=\text{CCl}_2$, is a readily polymerizable liquid (b.p. 31.7 °C). It is manufactured on a relatively small scale from 1,1,2-trichloroethane by elimination of HCl using milk of lime or by a thermal means. Vinylidene chloride is used as a monomer and for the production of methylchloroform.

The thermal elimination of HCl from 1,1,2-trichloroethane yields *cis*- and *trans*-1,2-dichloroethylenes, $\text{ClCH}=\text{CHCl}$ (liquids, b.p. 60.3 and 47.5 °C); the yield of these products is 35-45 percent. They are used as low-boiling solvents and extractants.

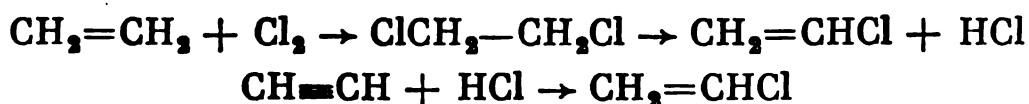
Trichloroethylene, $\text{CHCl}=\text{CCl}_2$ (a liquid, b.p. 87 °C) is widely used as a nonflammable solvent of low toxicity. It is produced from tetrachloroethanes (from 1,1,2,2- or 1,1,1,2-isomers) by the elimination of HCl using $\text{Ca}(\text{OH})_2$ or by a thermal means.

Tetrachloroethylene or *perchloroethylene*, $\text{CCl}_2=\text{CCl}_2$ (b.p. 121 °C) is an extensively used noncombustible solvent of low toxicity. It is manufactured from pentachloroethane by the same methods.

The chloro-olefins mentioned above are also produced currently by other methods, which are described below.

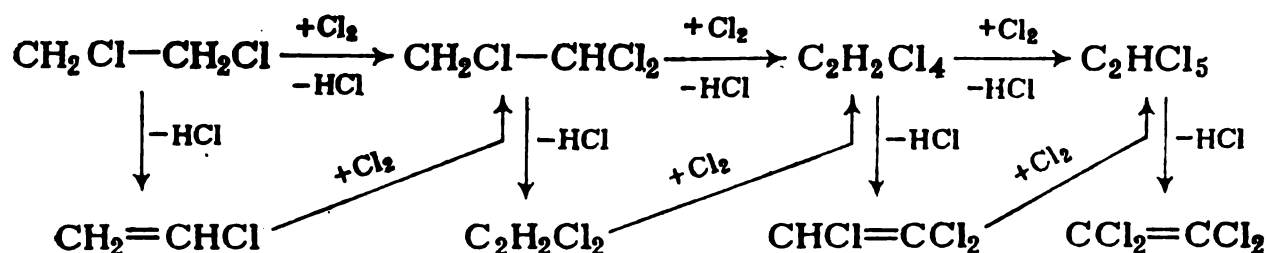
Thermal dehydrochlorination is accomplished at about 500 °C (for dichloroethane) and at 400-450 °C (for tri-, tetra- and pentachloroethanes)—either only thermally or in the presence of a small amount of chlorine (as initiator) and heterogeneous catalysts. Since the process is endothermic, it is carried out in tubular reactors heated by flue gases (say, in a tubular furnace, just as in the pyrolysis of hydrocarbons).

This process employed for the production of vinyl chloride has proved to be 30 and 14 percent more economical than the alkaline dehydrochlorination of dichloroethane and the hydrochlorination of acetylene described earlier. The manufacture of vinyl chloride has been made cheaper by combining two routes of its synthesis—from ethylene and acetylene when the HCl liberated in the pyrolysis of dichloroethane is utilized for the hydrochlorination of acetylene:



In this reaction, half of the acetylene is replaced by less costly ethylene, and hydrogen chloride is employed efficiently in the same process with complete use of nearly all of the starting chlorine. This has further reduced the cost of vinyl chloride by 6-7 percent.

Further, a combined chlorination-dehydrochlorination process has been worked out for the production of tri- and tetrachloroethylenes. Instead of the preliminary synthesis of tetra- or pentachloroethanes, this process combines in a single reactor the thermal chlorination of 1,2-dichloroethane and the elimination of HCl from the chloro derivatives:



Depending on the molar ratio of chlorine to dichloroethane, mixtures of varying composition are produced, including those with a preponderance of di-, tri- or perchloroethylenes or with these being produced in the ratio desired; the other chlorination products may be returned to the reaction. As a result, the investment cost has been reduced and, besides, the heat of the exothermic chlorination reaction is efficiently utilized to compensate for the negative heat effect of

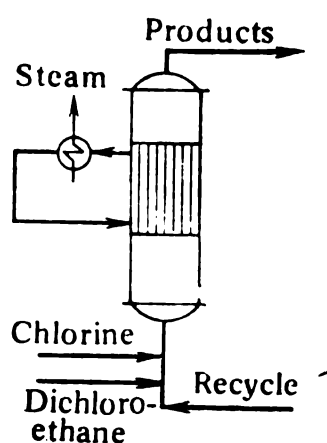


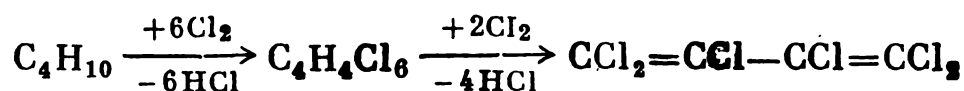
Fig. 2.18. Reaction unit for the combined chlorination and dehydrochlorination of 1,2-dichloroethane with production of tri- and tetrachloroethylenes.

HCl elimination. Such a combined process can be carried out in a hollow reactor or in an apparatus with a fluidized-bed refrigerant, the excess heat being removed by recycling the unchlorinated compounds and tetrachloroethylene or by cooling with a boiling heat carrier, which generates steam of the required parameters in the waste-heat boiler (Fig. 2.18).

Analogous processes are employed for the manufacture of some higher chloro-olefins.

Hexachlorobutadiene, $\text{CCl}_2=\text{CCl}-\text{CCl}=\text{CCl}_2$, is used as a

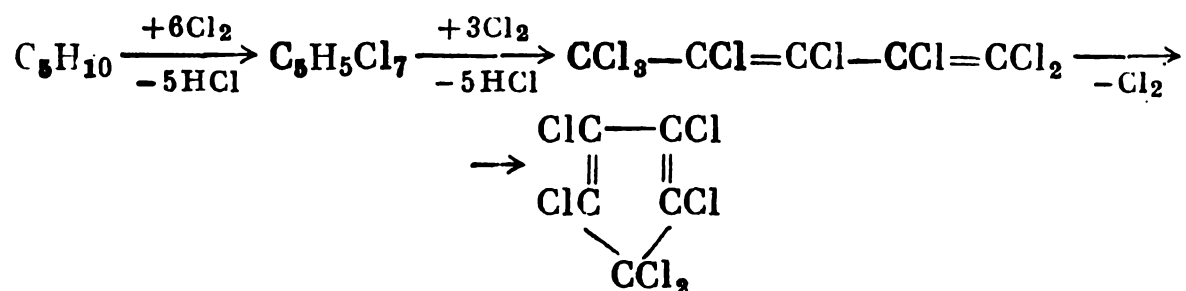
insecticide. It is produced by a two-step process from *n*-butane or *n*-butylenes or their mixtures. They are first chlorinated in the liquid phase by a radical-chain mechanism, the product having the general formula $\text{C}_4\text{H}_4\text{Cl}_6$. Then, the combined chlorination and dehydrochlorination of this product is carried out in the reactor with a fluidized bed of a heterogeneous catalyst:



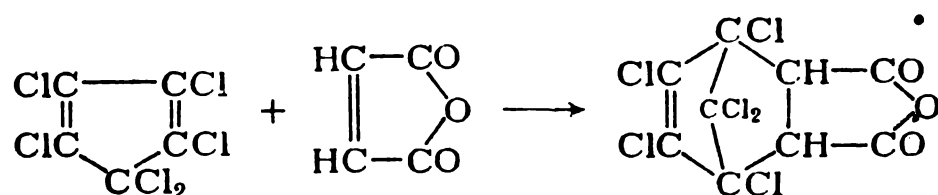
It proves impossible to pass the C_4 fraction into the last reactor because of the evolution of a large amount of heat, which is why the process is carried out in two steps.

Hexachlorocyclopentadiene, C_5Cl_8 , is produced by the two-step chlorination of cyclopentadiene or pentane-amylenes fractions. First, for the same reason as in the preceding case, liquid-phase chlorination is accomplished, which yields a product with an approximate general formula, $\text{C}_5\text{H}_5\text{Cl}_5$ or $\text{C}_5\text{H}_5\text{Cl}_7$. Then, in a tubular unit or in a reactor with a fluidized bed of the catalyst (or of a heat carrier) there is carried out a combined process of chlorination and HCl elimination using a pentane-amylenes fraction, this being followed by the cyclization

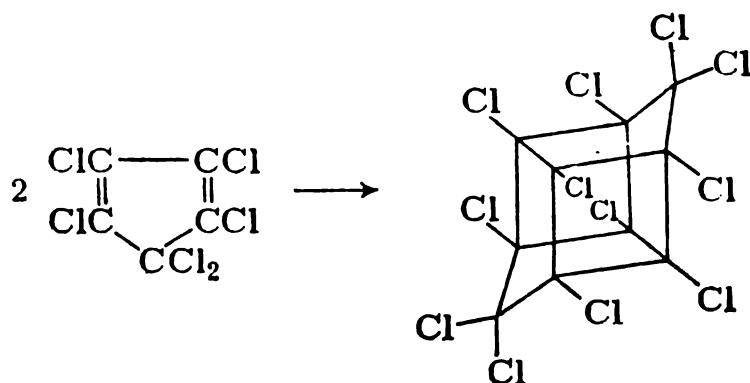
zation of the product at one of the intermediate steps:



Hexachlorocyclopentadiene is a valuable intermediate. It is used together with maleic anhydride as the feedstock for the diene synthesis of *chlorendic anhydride*, which is a monomer for the production of nonflammable or self-extinguishing polymers:

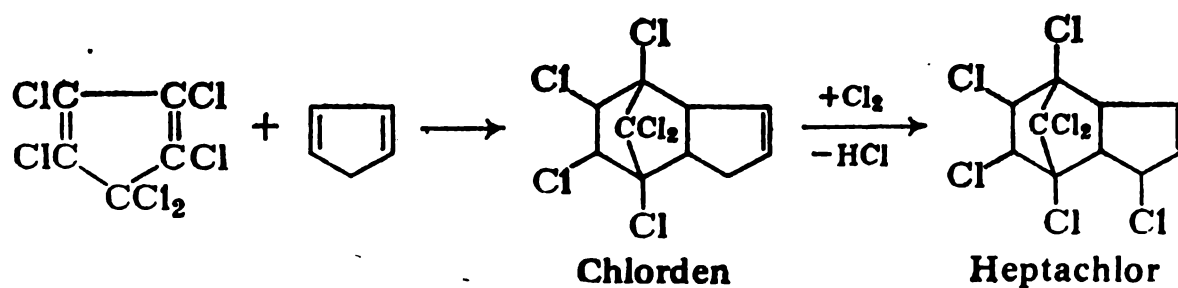


The dimerization of hexachlorocyclopentadiene in the presence of aluminium chloride gives a compound called Myrex:



Myrex is used as an insecticide, plasticizer and fire-resistant additive to various polymeric materials.

Hexachlorocyclopentadiene is also the basic component of many other pesticides, but most of these pesticides have proved unsuitable because of the high toxicity and tendency to be accumulated in living organisms and soil. Exceptions are a few derivatives, of which mention should be made of *heptachlor* (3,4,5,6,7,8,8a-heptachlorodicyclopentadiene). It is produced by the diene synthesis with cyclopentadiene and subsequent chlorination of the chlordene formed at a low temperature in the presence of a catalyst:



Processing of Chloro-Organic Wastes. It has already been mentioned that chlorination processes often give organic by-products, which do not find specific application. In order to develop wasteless technology it has been suggested that these by-products be burned off with the HCl being regenerated but with all of the carbon being lost in the form of CO_2 . More efficient processes have been developed in recent years, which are the basis for modern methods of production of carbon tetrachloride and tetrachloroethylene.

Various chloroaliphatic wastes are subjected to high-temperature chlorination in the gas phase. In this process, tetrachloroethylene is produced from the C_2 compounds by the above-described combined

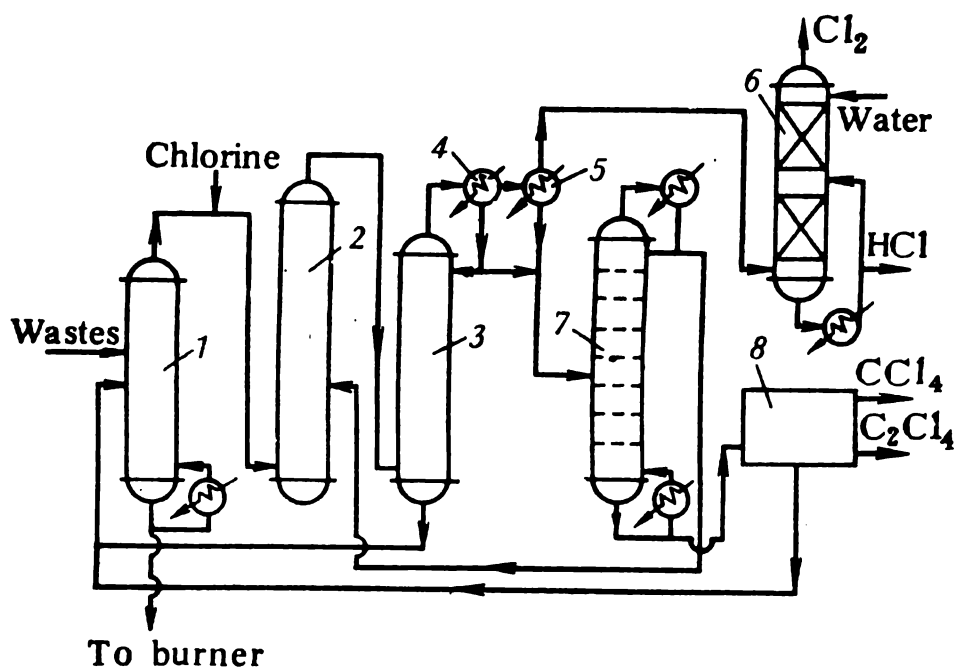
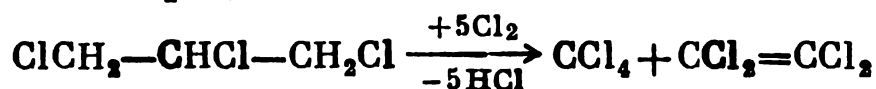


Fig. 2.19. Flow diagram of production of carbon tetrachloride and tetrachloroethylene from chloro-organic by-products:

1—vaporizer; 2—reactor; 3—quench column; 4, 5—coolers; 6—HCl absorber; 7—dry-neutralization column; 8—fractionating unit.

process of chlorination and HCl elimination. In an analogous treatment of wastes of C_3 and higher compounds these reactions are combined with pyrolysis at the carbon-carbon bond, which leads to CCl_4 and C_2Cl_4 ; for example,



The by-products formed are the condensation products (hexachlorobutadiene, hexachlorobenzene), which under these conditions do not undergo chlorinolysis; they are discarded.

The flow diagram of the production of carbon tetrachloride and tetrachloroethylene from chloro-organic wastes is given in Fig. 2.19. A mixture of wastes is led to vaporizer 1, in which the heavy products are separated and sent for burning. The vapours of chloro-organic compounds are mixed with excess chlorine (10-15 percent of the

chiometric amount) and led to reactor 2. The reactor is a hollow d apparatus, which may contain a fluidized bed of a heat exchange lium (quartz sand). Because of the very high exothermicity of overall process the excess heat is removed by introducing the re- e crude product into the reactor and by maintaining the tem- ture at 500-590 °C. The hot vapour-gas mixture from the reactor ed to quench column 3, where the temperature is lowered down 100-145 °C by refluxing with the liquid condensate from water er 4. The heavy products are collected in the still and returned vaporizer 1. The gaseous mixture is additionally chilled in brine er 5, separated from the condensate and sent to column 6 for the orption of HCl by water, as a result of which 30-percent hydro- ric acid is formed and the chlorine is simultaneously separated may be returned to the reaction or used for other purposes.

oth condensates from coolers 4 and 5 are sent to column 7, where HCl and Cl₂ dissolved in it are distilled off together with a certain ion of chloro-organic products, which are returned to reactor 2 emove excess heat. The liquid products from the still of column 7 subjected to two-stage fractional distillation to produce carbon achloride and tetrachloroethylene in the form of distillates, the due from the distillation being returned to vaporizer 1.

arious chloro-organic wastes (including the heavy residues left n the preceding refining operation and the cyclic chloro-organic ducts that do not lend themselves to gas-phase pyrolysis and also gen-containing compounds) can be subjected to chlorinolysis. he liquid phase at 500-600 °C and 20 MPa, the contact time being ut 20 min. A single pass through the hollow reactor, which is de- ed for operation at high pressures and temperature, yields carbon achloride, hexachloroethane, hexachlorobenzene, and the oxygen- taining compounds give phosgene. After the mixture is throttled heavy products are separated and returned to the reaction; from remainder there are recovered carbon tetrachloride, phosgene, rine (which is returned to the reaction) and anhydrous hydrogen ride.

he above-described two methods of processing chloro-organic tes have been developed relatively recently but have become ustrially important because they solve the problem of the simul- ous synthesis of CCl₄ and C₂Cl₄.

2. Oxidative Chlorination and Synthesis Chloro Derivatives Combined h Oxidative Chlorination

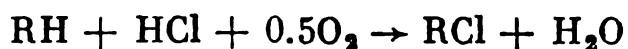
All the substitutive chlorination and pyrolysis processes that have n described for chloro derivatives involve the formation of HCl, ich is utilized in the form of hydrochloric acid and occasionally

for hydrochlorination. These routes for the use of HCl are, however, limited, in particular because of the insufficient purity of the hydrochloric acid formed and because its overall production exceeds its consumption. Therefore, the problem of the more complete use of chlorine, its replacement by HCl or suppression of the formation of by-product HCl has assumed increasing importance for the economic development of chloro-organic industries. This problem is solved with the aid of oxidative chlorination (or oxychlorination).

Oxidative Chlorination. This process is based on the well-known Deacon reaction:

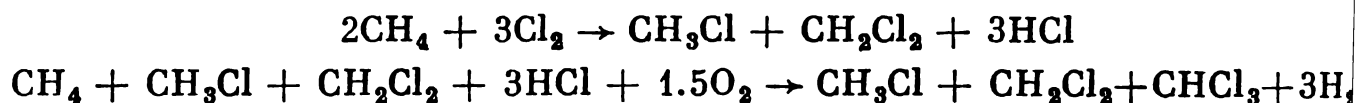


Since the reaction is exothermic, its equilibrium is shifted to the right with decreasing temperature, but the known catalysts based on cupric chloride enable the reaction to be carried out only at 200–400 °C. Chlorination reactions proceed under the same conditions and when the two processes are combined in a single apparatus, oxychlorination occurs with the aid of HCl and O₂, which becomes irreversible:



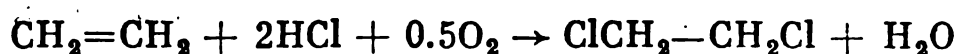
The basic reaction is accompanied by the side oxidation of the hydrocarbon by oxygen, the hydrolysis of the chloro derivatives by steam and dehydrochlorination. It is for this reason that the process can be used only for very stable reagents, primarily for methane, ethylene, benzene and, to a lesser extent, for ethane. It was used originally for the production of phenol via the oxidative chlorination of benzene, but this Raschig process has lost its value. It is only in recent years that the method has been revived for lower aliphatic hydrocarbons.

The oxidative chlorination of methane involves only substitution reactions; depending on the reactant ratio, mixtures of chloro derivatives of varying composition are obtained. Since CCl₄ is now more economical to produce from chloro-organic wastes, the oxychlorination of methane is accomplished for the synthesis of the end products CH₂Cl₂ and CHCl₃. Here, the direct chlorination of methane is combined with the oxychlorination of the resulting mixture by the hydrogen chloride present in it:

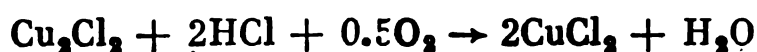


As a result, the chlorine is used completely and no HCl is formed.

The oxidative chlorination of ethylene at 240–280 °C involves the addition of chlorine at the double bond rather than substitution:



It has been found in this particular case that the chlorination is effected not by chlorine but directly by cupric chloride, which is regenerated by the action of HCl and O₂:



Probably, oxygen oxidizes Cu₂Cl₂ to cupric oxychlorides, which are converted to CuCl₂ with the aid of HCl.

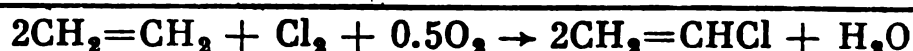
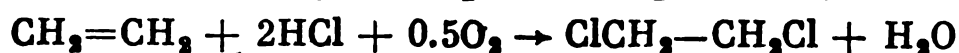
Oxychlorination catalysts are prepared by impregnating the supports (pumice, corundum, aluminosilicate) with salts with subsequent drying. The main component of the catalysts used is cupric chloride; to reduce the volatility, KCl is added, which forms complexes with CuCl₂. Various modifiers have been proposed, including compounds of rare-earth elements.

An important feature of the process is its very high exothermicity, which requires heat exchange in the reactor. The medium is not very aggressive and heat exchangers may be made of special steel and at a temperature below 250 °C carbon steel may even be used. The most frequently used reactors are those containing a fluidized catalyst bed; the reactor is supplied with cold reagents, and the excess heat is removed by an internal heat exchanger due to the evaporation of the water condensate with generation of steam of the corresponding pressure. Reactors with a fixed catalyst bed are also employed; they are made as shell-and-tube units described earlier for the hydrochlorination of acetylene.

The oxidizing agent commonly used is air, the reaction being carried out at 0.3-1 MPa to reduce the volume of the apparatus and manifolds and also to provide a better recovery of the products. It is also recommended that technical oxygen be used as an oxidizing agent for the same purpose, which enables the recirculation of the unconverted compounds. Oxygen is usually used in a slight excess (about 5 percent) with respect to the amount required stoichiometrically for the oxidation of HCl. The molar ratio of HCl to the organic reagent depends on the number of chlorine atoms to be introduced into the molecule. The degree of conversion of HCl and oxygen reaches 80-90 percent; 2 to 5 percent of the hydrocarbon feed is burned to CO₂.

Technology of Chlorine-Balanced Synthesis of Vinyl Chloride from Ethylene. The most important of the processes involving oxidative chlorination is the so-called balanced method of production of vinyl chloride from ethylene. It is a combination of three processes: direct additive chlorination of ethylene to 1,2-dichloroethane; thermal dehydrochlorination of 1,2-dichloroethane to vinyl chloride; and oxidative chlorination of ethylene to 1,2-dichloroethane with the aid

of HCl formed upon dehydrochlorination:



As a result, vinyl chloride is obtained from ethylene, chlorine and oxygen, the chlorine being completely used and no HCl being formed.

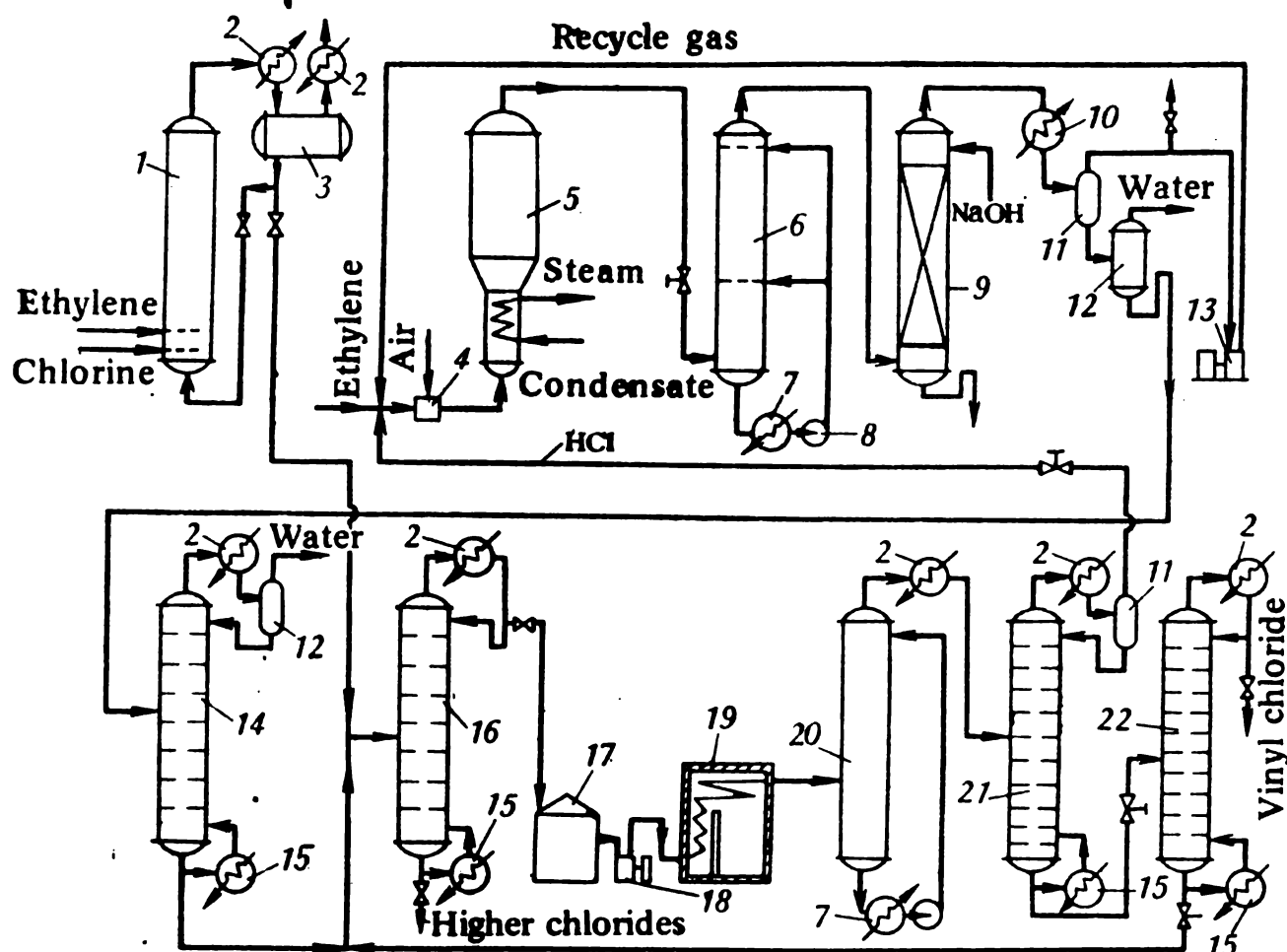


Fig. 2.20. Flowsheet for synthesis of vinyl chloride by the combination method: 1—chlorinator; 2—condenser-coolers; 3—dichloroethane collector; 4—mixer; 5—oxychlorinator; 6, 20—direct-mixing coolers; 7, 10—coolers; 8—circulation pump; 9—scrubber; 11, 12—separators; 13—compressor; 14—drying column; 15—boilers; 16, 21, 22—fractionating columns; 17—storage tank; 18—pump; 19—tubular furnace.

This method obliterates the need to use costly acetylene and is at present the most economical method for the synthesis of vinyl chloride: the cost of the monomer produced is reduced by 25-30 percent as compared with the hydrochlorination of acetylene.

The flow diagram of the process is given in Fig. 2.20. The direct chlorination of ethylene to 1,2-dichloroethane is carried out in column chlorinator 1, into which chlorine and ethylene are fed through the corresponding bubblers. In the column the liquid in which the catalyst (FeCl_3) has been dissolved is kept at a constant level. The reaction heat is removed by evaporation of dichloroethane; its vapours are condensed in condenser-cooler 2. The condensate is

passed to collector 3 and part of it is returned to the column (in order to maintain normal thermal conditions in the chlorinator and a constant level of the liquid), the remainder being sent to fractionation. In collector 3 the residual gases are separated from the condensate and additionally cooled with brine in cooler 2 to prevent the loss of dichloroethane and discharged to the atmosphere.

The oxychlorination step is carried out in reactor 5 containing a fluidized bed of catalyst under a pressure of about 0.5 MPa and at 260-280 °C. Ethylene, the recycle gas and hydrogen chloride are mixed in the tube, following which technical oxygen is added to them in mixer 4. The manner in which the mixing is effected and the composition of the mixture must provide operating conditions that do not present explosion hazard. In reactor 5 the evolved heat is removed by evaporation of the water condensate under pressure; as a result, process steam is generated, which is used in the same plant. The reaction gases, which consist of the unconverted ethylene, oxygen and hydrogen chloride and also of dichloroethane vapours and impurities of inert gases, are chilled in cooler 6 by a water-dichloroethane mixture circulating through cooler 7. The partially cooled gas-vapour mixture is freed from HCl and CO₂ in hot caustic scrubber 9 and cooled completely in cooler 10. The condensate is separated from the gas in separator 11, following which the recycle gas (a mixture of ethylene, oxygen and inert substances) is returned by compressor 13 to oxychlorination.

Part of the gas is withdrawn into the general off-gas line (after the volatile chloro-organic substances are recovered and after sanitary purification) in order to avoid excessive accumulation of inert impurities and discharged into the atmosphere. The condensate from separator 11 goes to separator 12, where the heavier dichloroethane is separated from water. It is used to dilute the caustic that purifies the gas in scrubber 9; this makes it possible to avoid losses for the dissolution of dichloroethane.

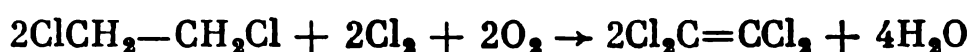
The dichloroethane resulting from the oxychlorination is saturated with water, which is why it is first of all dehydrated in column 14 by azeotropic drying; this column is fitted with boiler 15, condenser 2 and separator 12. The dichloroethane stream (from the direct chlorination and oxychlorination stages) is combined with the stream of dichloroethane that has not been converted upon pyrolysis. In fractionator 16 high-purity dichloroethane is distilled off from the higher chlorides and collected in tank 17.

The pyrolysis of dichloroethane to vinyl chloride and HCl is carried out in tubular furnace 19 at 1.5-2 MPa and 500 °C. The reaction gases are chilled in cooler 20 by circulating dichloroethane and then in condenser-cooler 2 by water, following which the mixture is passed to fractionating column 21 fitted with a boiler, a condenser-cooler and separator 11. The pressure in the column enables the condensation

of hydrogen chloride as a reflux and the most efficient purification of the product from HCl, as a result of which HCl is obtained in a dry and pure state. This gaseous HCl is then passed to oxychlorination. The still liquid of column 21, which consists of vinyl chloride and the unconverted dichloroethane, is sent to column 22, where it is distilled off from the unconverted dichloroethane (which is returned to fractionation) under a pressure that provides the condensation of vinyl chloride.

The vinyl chloride produced is 99.9 percent pure and is quite suitable for further polymerization.

Processes Based on the Combination of Oxidative Chlorination and Cleavage of Chloro Derivatives. In the synthesis of vinyl chloride considered above the oxychlorination and elimination of HCl were conducted separately in two reactors. But, when the temperature is raised to 400–450 °C it becomes possible to carry out the two processes in a single reactor and to compensate more than sufficiently for the heat consumed for the elimination. Based on this principle is one of the most efficient current methods of producing tri- and tetrachloroethylenes from 1,2-dichloroethane or other C₂ chloro derivatives:



As compared with the combined chlorination and dehydrochlorination of dichloroethane (see Sec. 2.4), this process differs favourably by a minimum consumption of chlorine and the absence of the formation of by-product HCl. Obviously, in this process, depending on the chlorine-to-dichloroethane ratio, a mixture of chloroethylenes is obtained, the insufficiently chlorinated compounds being returned to the reaction. The process may also be carried out in such a way that it will result in the simultaneous formation of tri- and tetrachloroethylenes using, as a raw material, not only dichloroethane but also various waste C₂ chloro derivatives. The process is accomplished in a reactor with a fluidized-bed catalyst, which is analogous to the catalyst used for the production of vinyl chloride, the excess heat being removed by the boiling water condensate and high-pressure steam generated. There exist industrial high-capacity plants designed for the joint production of tri- and tetrachloroethylenes by this particular process. When this process is used for the manufacture of tetrachloroethane, there is no need to add chlorine to the reaction:



Of some interest is the Transcat process developed recently for the production of vinyl chloride from ethane or its mixtures with ethylene. A distinctive feature of this process is that the reaction is carried out in a molten catalyst used for oxychlorination and the chlorination

of organic compounds is effected separately from the oxidation of the melt, owing to which no side oxidation of ethane occurs and the products are not diluted with nitrogen, which facilitates their recovery. The flow diagram of the Transcat process is shown in Fig. 2.21. In reactor 1 the spent catalyst melt is oxidized by air. Besides, the HCl-containing gases are introduced from furnace 2 into reactor 1 for the pyrolysis of chloro-organic wastes. The following reactions take place:



The regenerated melt, which still contains cupric oxychlorides, is transferred to reactor 3, into which are introduced fresh feedstock

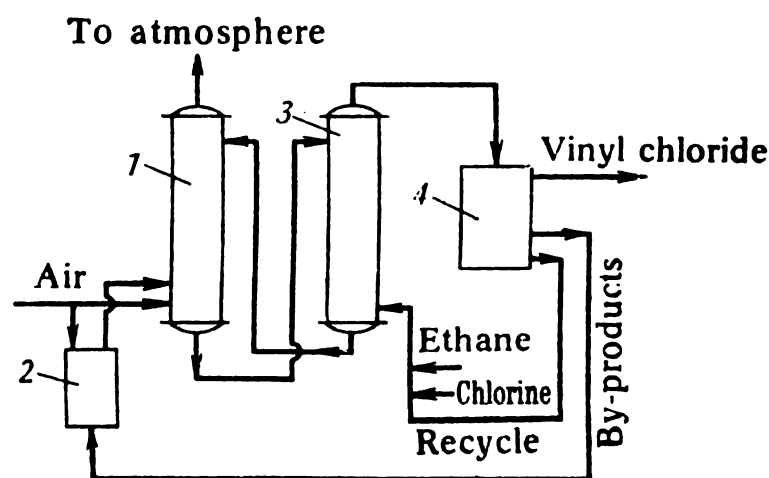
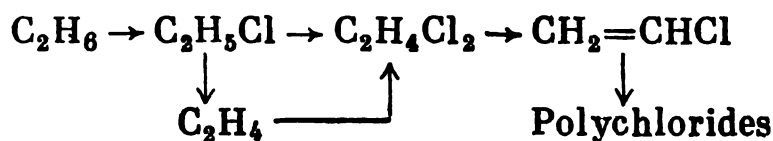


Fig. 2.21. Flowsheet of the Transcat process for production of vinyl chloride: 1—melt oxidation reactor; 2—by-product pyrolysis furnace; 3—oxidative chlorination reactor; 4—fractionating unit.

(ethane and chlorine) and the stream recycled after the products are separated and composed of ethane, ethylene, ethyl chloride and dichloroethane. In this reactor, the following reactions take place, which involve the chlorine introduced and CuCl_2 :



and the HCl formed converts cupric oxychlorides to CuCl_2 . The products are separated by fractional distillation with the recovery of 99.9-percent pure vinyl chloride, the recycle and higher chlorides, which are passed to furnace 2 for combustion. The yield of vinyl chloride is 80 percent on ethane and 99 percent on chlorine. The spent melt is again transferred to reactor 1 for oxidation.

In spite of the use of the cheapest raw material (ethane), the process under consideration has a serious disadvantage: a complicated system of recycling of large quantities of the molten catalyst is required. Of interest are therefore other methods of conversion of ethane and ethane-ethylene mixtures into organic chlorine products. They are

based on the combination or coupling of direct and oxidative chlorination reactions with the elimination of HCl and with other reactions. For example, in one process, which has been employed on an industrial scale, in reactor 1 (Fig. 2.22) the direct chlorination of ethane (or ethane-ethylene mixtures) is combined with the elimination of HCl from the chloro derivatives. In unit 2 the major products (vinyl chloride, vinylidene chloride) are recovered from the first-stage products, the remaining compounds, including ethylene, the unconverted ethane and HCl, being sent to reactor 3 for oxychlorination. Here,

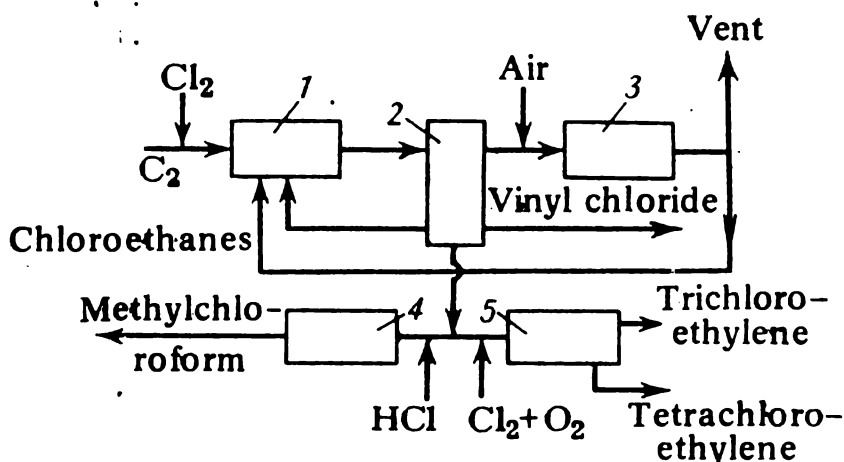


Fig. 2.22. Combined processing of ethane or ethane-ethylene mixtures: 1—thermal chlorination and dehydrochlorination; 2—fractionation; 3—oxidative chlorination; 4—hydrochlorination; 5—oxidative chlorination and dehydrochlorination.

chloroethanes are produced, which are separated from air and returned to reactor 1. The process is combined with the hydrochlorination of vinylidene chloride for the production of methylchloroform and with the oxidative chlorination of all by-product chloro-organic compounds to tri- and tetrachloroethylenes.

Thus, new industrial processes combined or coupled with the splitting of chloro derivatives and with oxidative chlorination, have a strong impact on the technology of synthesis of the largest multitonnage organic chlorine products, on the economical efficiency of these industries and on environmental protection. Such processes are now being intensively developed and put into industrial practice; they gradually supersede the older and less efficient processes.

2.5. Fluorination Processes

The following reactions involving the introduction of fluorine atoms into molecules of organic compounds are of commercial importance:

1. The action of molecular fluorine and certain metal fluorides in their highest valence state (CoF_3 , AgF_2); this involves mainly the replacement of hydrogen atoms in organic compounds by fluorine.

2. The action of hydrogen fluoride and its salts, in which the metal atoms are in a normal valence state (AgF , HgF_2 , SbF_3); fluorine is mainly substituted for chlorine atoms and the intermediate step of preparation of fluorine organic compounds is chloro-organic synthesis.

5.1. Fluorination by Molecular Fluorine and Higher Metal Fluorides

The direct action of fluorine on organic compounds leads to a violent reaction accompanied by flashes and explosions. This results in the formation of hydrogen fluoride and the decomposition products of organic molecules (carbon black, carbon tetrafluoride). This direction of the reaction is due to its high exothermicity, which by far exceeds the dissociation energy of the carbon-carbon bond (see sec. 2.1).

The reaction proceeds less vigorously when fluorine (and vapours of an organic compound) is diluted under given conditions with a gas that takes on part of the heat evolved, thereby making the system operate outside the wide explosive limits. Such a diluent gas is commonly nitrogen. In liquid-phase fluorinations, use may be made of solvents stable to the action of fluorine (such solvents are fluorocarbons or, at low temperatures, carbon tetrachloride). In gas-phase fluorination reactions, which are most widely employed, apart from dilution with nitrogen, a positive effect is exerted by a heat-conducting packing (say, one made of a copper wire).

The mechanism of fluorination differs strongly from that of chlorination. This is accounted for by the very weak electrophilic nature of the fluorine molecule, which is why only radical-chain reactions take place. No initiators are needed for such reactions; the chain is initiated spontaneously due to the interaction of fluorine with a hydrocarbon:



Chain propagation occurs in a usual way:



A further distinctive feature is the high activity of fluorine and, as a consequence, its low selectivity upon its attack on an organic molecule. For example, in contrast to chlorination, fluorination reactions are accompanied by substitution and addition; the various hydrogen atoms are replaced with nearly equal probability, including those present in the fluoro derivatives formed. Moreover, the carbon-carbon bond cleavage is widely encountered. These conversions can be limited by employing milder reaction conditions.

For the reasons mentioned above, fluorination is carried out on an industrial scale for the production of perfluoro derivatives of hydro-

carbons (perfluorocarbons), which are noted for their very high thermal and chemical stability. The fluorination products of middle petroleum fractions are used as thermally stable lubricating oils and hydraulic fluids, and the derivatives of the C_7 - C_9 fraction are used as solvents.

Fluorination Technology. The fluorination processes employed on an industrial scale are as follows.

Catalytic fluorination is accomplished in an apparatus containing copper filings covered with a layer of silver: fluorine and a hydrocarbon diluted with nitrogen are introduced into the apparatus. The

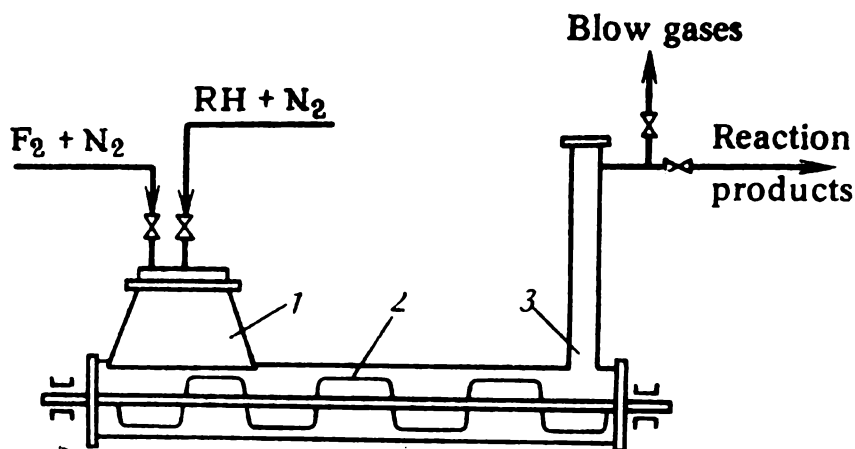
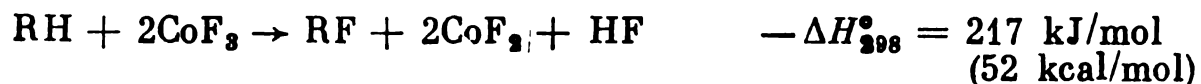


Fig. 2.23. Reactor for metallofluoride fluorination:
1—charging door; 2—impeller mixer; 3—discharge pipe.

role of copper, which is noted for its high thermal conductivity, is to accumulate the heat evolved. Silver is presumably converted under the action of fluorine to AgF_2 , which fluorinates hydrocarbons sufficiently mildly. However, a direct interaction of the hydrocarbon with fluorine also takes place, as a result of which the yield of the final product is relatively low, ranging from 40 to 80-90 percent.

The *metal-fluoride process* is employed most extensively for industrial organic synthesis. It is based on the use of higher metal fluorides (CoF_3 , MnF_3), which interact with hydrocarbons relatively mildly and with the evolution of a moderate amount of heat:



The spent salt is again regenerated by the action of fluorine:



In this way, the total heat of the reaction between F_2 and RH , which is equal to 460 kJ/mol, is distributed between two steps; the hydrocarbon takes part only in a step that has a moderate heat effect. As a result, the yield of the product is high.

The reaction unit (Fig. 2.23) is a horizontal steel tube with an impeller mixer, which rotates at a speed of around 20 rpm. The

be is nearly half-filled with cobalt fluorides. Vapours of the organic agent diluted with a 5- to 10-fold excess of nitrogen are introduced to the left part of the tube fitted with a charging door. The products formed are first passed to the discharge pipe, where they are freed from the entrained particles of cobaltic fluoride, and then to cooling and separation units, following which they are withdrawn from the other end of the tubular reactor.

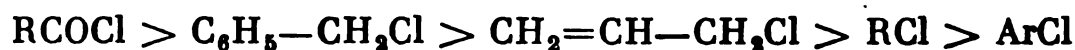
The reaction is continued until 50 percent of cobalt trifluoride is converted to the difluoride. The temperature maintained at the inlet 150-200 °C and the outlet temperature ranges from 300 to 380 °C. This temperature difference is accounted for by the fact that the hydrocarbon is fluorinated sufficiently rapidly and in order to avoid its breakdown a low temperature is desirable. At the same time, the placement of the last hydrogen atoms proceeds with great difficulty, and a higher temperature is required. The optimum contact time is 3 min. After 50 percent of cobalt trifluoride is used up, the hydrocarbon supply is discontinued and the reactor is blown with nitrogen. The cobalt trifluoride is then regenerated by passing free fluorine diluted with nitrogen at 250 °C; the reactor is again blown with nitrogen in order to remove traces of fluorine and the reaction is started anew. Thus, the reactor operates batchwise and the operation consists of two basic stages (the fluorination reaction and regeneration) and two blow-off runs. This is a substantial shortcoming of the process.

Electrochemical fluorination has been developed only recently, but has a number of advantages over the methods described above. The essence of the process is as follows: upon electrolysis of anhydrous hydrogen fluoride (with metal fluorides added to increase the electrical conductivity) the fluorine evolved on the anode reacts immediately with the organic compound dissolved or emulsified in a liquid. Since the reactions occur in the liquid phase with the reaction mass being stirred, good heat conduction is achieved and the process can be controlled in various ways. To carry out this process, there is no need to prepare and purify molecular fluorine, because it is generated industrially by electrolysis. The best results are provided by electrochemical fluorination in the synthesis of perfluoro substituted carboxylic acids, ethers, esters, amines, sulphides, and other compounds that are soluble in liquid hydrogen fluoride.

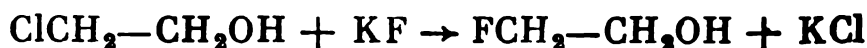
5.2. Fluorination by Hydrogen Fluoride and Its Salts. Production of Fluoro-Olefins

The ability to lose chlorine atoms and add on fluorine is exhibited by chloro derivatives having a sufficiently mobile halogen atom. Depending on the structure, chloro derivatives are arranged in the

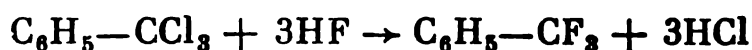
following order of increasing reactivity:



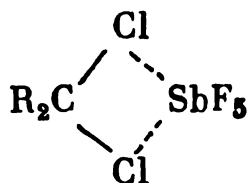
The replacement of chlorine atoms in sulpo chlorides, acid chlorides of carboxylic acids and chlorohydrins can be accomplished using potassium fluoride:



The reactive chlorine atoms in chlorosilanes, acid chlorides and chloro derivatives with a halogen atom in the alpha-position relative to the aromatic ring or the vinyl group are also smoothly replaceable by the action of anhydrous hydrogen fluoride:

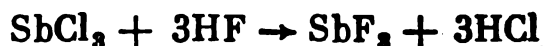


In order to replace less mobile halogen atoms in the laboratory use is made of silver, mercury and antimony fluorides (AgF , HgF_2 , SbF_3). Antimony trifluoride has found widest application. It can replace a chlorine atom in monochloroalkanes and is used only in reactions involving chloro derivatives that have at least two halogen atoms attached to one carbon atom. It has been found that the reactivity of antimony trifluoride can considerably be increased by addition of antimonous chloride or fluoride or by introduction of chlorine which converts part of the reagent to the pentavalent state. This is presumably associated with the formation of complexes; the fact that the reaction is feasible only with chloro derivatives having at least two halogen atoms at one carbon atom leads one to deduce the following structure of the complexes:

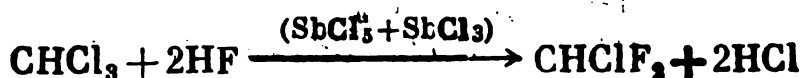


The subsequent reaction leading to substitution can be accomplished as a result of the carbon-chlorine and the antimony-fluorine bonds being weakened.

The antimonous chlorides formed can be converted to fluorides by the action of hydrogen fluoride and again used for fluorination:

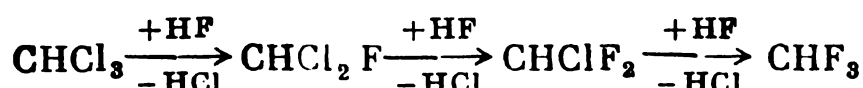


The two processes—the replacement of chlorine atoms in chloro derivatives and the regeneration of antimony halides—can be conveniently combined. Here, the overall effect boils down to the replacement of chlorine atoms using hydrogen fluoride, when antimony chlorides and fluorides play the role of catalysts or, more precisely, of fluorine carriers:



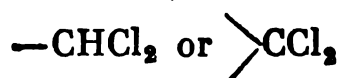
reaction is most extensively used on an industrial scale, since it considerably simplifies the process, enabling it to be accomplished in one step in a single apparatus. With hydrogen fluoride and the chloro derivative being fed continuously and with continuous removal of hydrogen chloride and reaction products the antimony halides present in the form of mixed chlorides and fluorides, say SbCl_3F_2 , SbCl_2F or SbCl_2F_3 and SbClF_2 . With this liquid catalyst it is possible to convert large amounts of the reactants, but the catalyst must be replenished with chlorine in order to compensate for the loss of antimononic halides as a result of their dissociation and side reactions.

The replacement of chlorine atoms proceeds in the same way as successive-parallel reactions and the composition of the products depends on the ratio of the reactants:

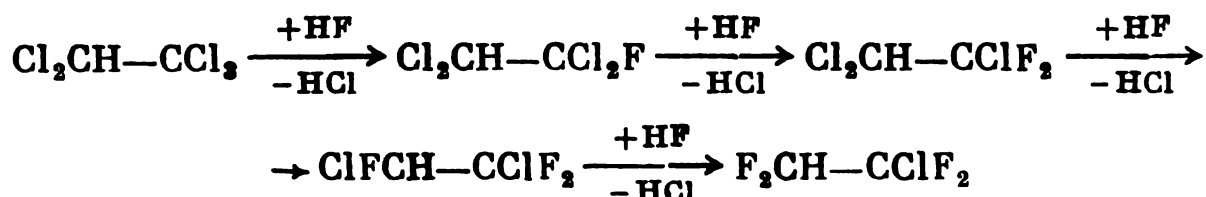


The yield of the products can nevertheless be easily controlled in a number of cases owing to the fact that upon successive substitution of fluorine for chlorine atoms the boiling point of the compounds obtained gradually falls. By carrying out the reaction at a certain temperature under a pressure such that the end product (say CHClF_2 in the preceding equation) could be distilled off from the reaction mixture as it is formed, it is possible to avoid the formation of more highly fluorinated compounds. At the same time the higher-boiling unfluorinated reagents are left in the liquid reaction mixture until they are converted to the more volatile end product. It is the volatility of the final product that governs the choice of the pressure in the synthesis of relatively volatile organic fluorine compounds.

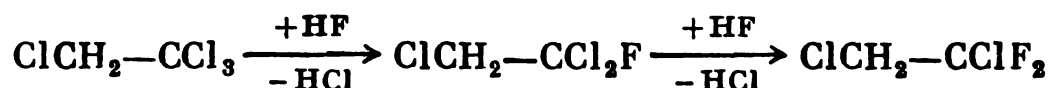
The choice of the temperature depends on the reactivity of the starting chloro derivative. For polychloroalkanes with a $-\text{CCl}_3$ group a temperature of about 100°C would suffice in order to replace one or two chlorine atoms; the third chlorine atom is replaced considerably more slowly. With chloro derivatives having less reactive groupings, such as



a higher temperature is required, say 150°C . For the reasons indicated the replacement of chlorine atoms in pentachloroethane proceeds in the following sequence:



and with unsymmetrical tetrachloroethane only two chlorine atoms are readily replaced:

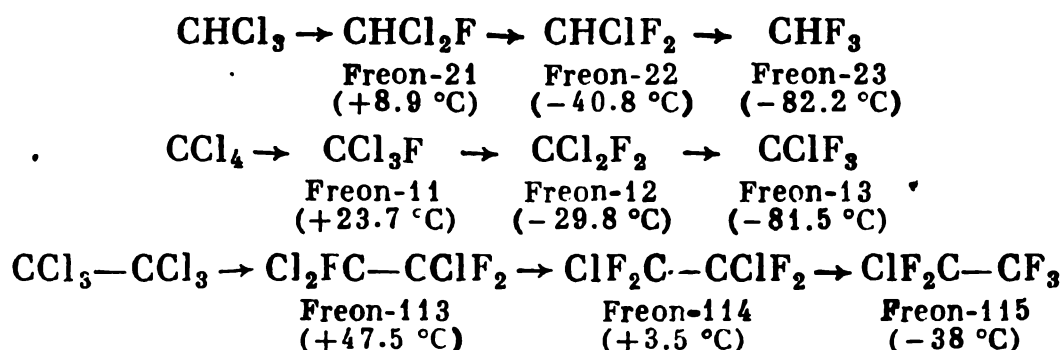


2.5.2.1. Freons

Freons are a group of polyhalogenated derivatives of methane and ethane containing fluorine and, in most cases, chlorine or bromine. They are gaseous compounds or low-boiling liquids having a mild, somewhat ethereal odour, are practically nontoxic, nonflammable and nonexplosive. These properties account for their extensive use in refrigeration and air-conditioning equipment. An important area of application of freons is the aerosol spraying of certain substances. Freons are also intermediates in the production of fluoro-olefins.

According to the chemical composition, freons are classified as Freon-11, Freon-12, Freon-13, Freon-113, etc. The last figure indicates the number of fluorine atoms, the second to the right the number of hydrogen atoms plus one, and the first to the left the number of carbon atoms less one. For example, Freon-12 has two fluorine atoms, one hydrogen, and only one carbon atom, which gives the formula CCl_2F_2 . Freon-113 is an ethane derivative with the formula $\text{C}_2\text{Cl}_3\text{F}_3$.

The most important freon compounds are manufactured on an industrial scale by the replacement of chlorine atoms with fluorine in chloroform, carbon tetrachloride, tetra-, penta- and hexachloroethane and methylchloroform. Below are given the names of some freons and their flash points (or boiling points) at atmospheric pressure:



The most popular freons in engineering are Freon-12 (dichlorodifluoromethane, CCl_2F_2), Freon-22 (chlorodifluoromethane, CHClF_2) and Freon-113 (trichlorotrifluoroethane, $\text{CCl}_2\text{F—CClF}_2$). For deep refrigeration use is made of low-boiling Freon-13 and Freon-23.

Production of Freons. As a typical example, we shall consider below the manufacture of dichlorodifluoromethane (Freon-12) from carbon tetrachloride and anhydrous hydrogen fluoride in the presence of antimony halides. The reaction is carried out at 100°C and at about 3 MPa; under this pressure CCl_4 , CCl_3F and HF are in the liquid state and CCl_2F_2 can be distilled as it is formed, which makes it

possible to prevent the formation of considerable amounts of CClF_3 .

The flow diagram of production of Freon-12 is shown in Fig. 2.24. Carbon tetrachloride and liquid hydrogen fluoride are pumped through flow meters 2 under pressure into reactor 3 containing a liquid catalyst (a mixture of antimonous and antimonic chlorides and fluorides diluted with the reactants and the unfluorinated product). Chlorine is also fed periodically in small amounts into reactor 3.

The reactor is a water-jacketed steel apparatus with an anticorrosive lining fitted with a reflux packed column 4 and a reflux condenser 5. The hydrogen chloride formed entrains vapours of the organic

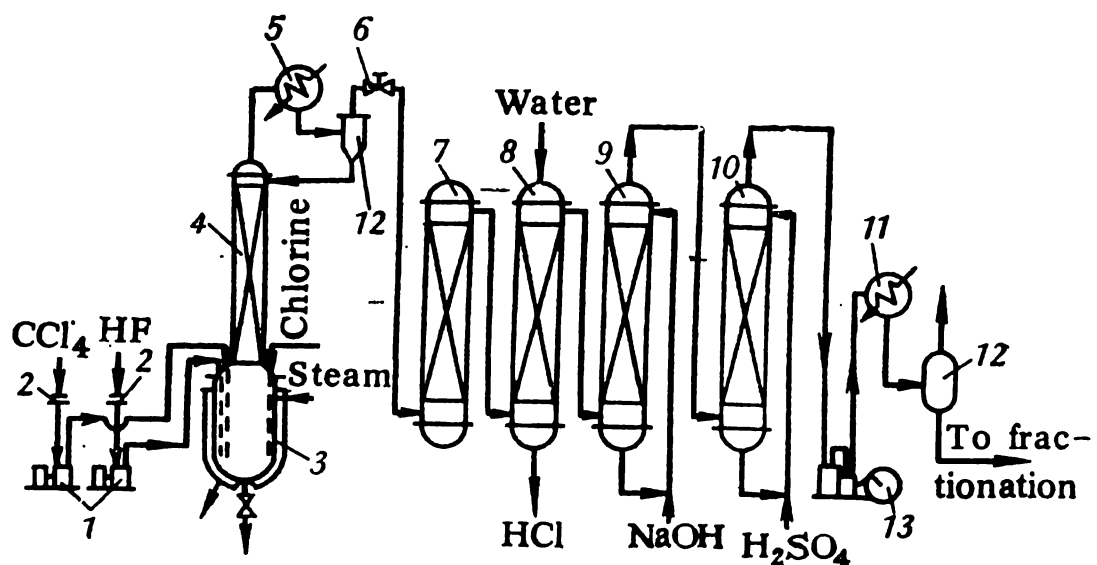


Fig. 2.24. Flow diagram of production of Freon-12:

—pumps; 2—flow meters; 3—reactor; 4—dephlegmating column; 5—reflux condenser; 6—throttle valve; 7—purification tower; 8—water scrubber; 9—caustic scrubber; 10—drying column; 11—brine cooler; 12—gas separator; 13—compressor.

compounds and hydrogen fluoride. In column 4 the vapours are partially condensed, the carbon tetrachloride and trichlorofluoromethane being returned to the reactor. To produce a reflux, part of dichlorodifluoromethane vapours are partially condensed in condenser 5 and returned to reflux column 4.

The vapour-gas mixture leaving condenser 5 consists mainly of hydrogen chloride and dichlorodifluoromethane with trichlorofluoromethane, chlorotrifluoromethane and hydrogen fluoride as impurities. After the pressure is lowered almost to atmospheric in throttle valve 6 the hydrogen fluoride is separated in tower 7 filled with lumps of potassium fluoride. The latter reacts with HF to form potassium [difluoride, KHF_2 , which can be used for the electrolytic production of fluorine. Further purification from the hydrogen chloride can be accomplished by the above-described method with the formation of concentrated hydrochloric acid. The flow diagram shows the simplest purification procedure through absorption by excess water in scrubber 8 and by aqueous caustic in scrubber 9. The remaining gas can be dried using concentrated sulphuric acid circulating in column 10.

The chlorofluoro derivatives are separated by low-temperature

fractionation. The vapours are compressed by compressor 13 to 1-1.2 MPa and cooled with brine in cooler 11 down to -10 to -15 °C. The condensate formed is passed to the separator which consists of several fractionating columns.

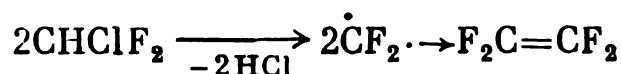
The light fraction consists of chlorotrifluoromethane (with a small amount of dichlorodifluoromethane) which is a by-product. The heavy residue left after fractionation contains trichlorofluoromethane, which is returned to the reactor. The major fraction of Freon-12 is produced in the liquid state under pressure. In order to use it as a refrigerant, it must be additionally dried—by freezing out the moisture or by treating with solid adsorbents, say with zeolites.

Gas-phase synthesis has been lately developed and industrially realized for the manufacture of freons from CCl_4 and HF in a fluidized bed of a heterogeneous antimony-based catalyst at 400 °C. It has been suggested that, just as in combined chlorination processes, the chlorination of a hydrocarbon (CH_4 , C_2H_6) be combined with the replacement of chlorine using HF . The reaction is carried out with the temperature being controlled by way of recycling the unconverted and insufficiently fluorinated chloro derivatives.

2.5.2.2. Fluoro-Organic Monomers

The most important fluoro-organic monomers are tetrafluoroethylene and monochlorotrifluoroethylene.

Tetrafluoroethylene, $\text{F}_2\text{C}=\text{CF}_2$ (a gas, b.p. -76.3 °C at atmospheric pressure) is manufactured on an industrial scale by the combined pyrolysis-condensation process described earlier (see Sec. 2.4.1). The feedstock is chlorodifluoromethane (Freon-22), which at 650-700 °C is converted to tetrafluoroethylene with evolution of hydrogen chloride:



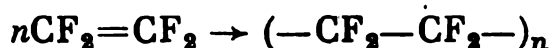
The elimination of fluorine occurs only to a slight extent (0.5-3 percent) because of the high bond dissociation energy of the carbon-fluorine bond. The pyrolysis by-products are fluoro-olefins with a higher molecular mass (C_3F_6 and C_4F_8) and also the products of the telomerization of tetrafluoroethylene with hydrogen chloride:



where n ranges from 2 to 17. A sufficiently good yield of tetrafluoroethylene (about 90 percent) is achieved when the pyrolysis is carried out in graphite, silver or platinum tubes and also with an incomplete (25- to 30-percent) conversion of chlorodifluoromethane.

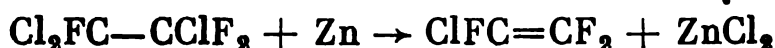
The polymerization of tetrafluoroethylene yields polytetrafluoroethylene, which was first produced in 1947 under the name of Teflon;

this country, the compound is known as Fluoroplast-4:

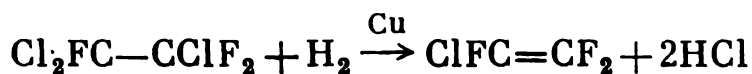


This polymer possesses excellent chemical stability, like all fluorocarbons, and high thermal stability. It is therefore used for the manufacture of various parts for chemical equipment and as a heat-resistant insulator.

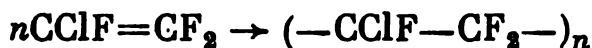
Monochlorotrifluoroethylene, $\text{ClFC}=\text{CF}_2$, is a gas (b.p. -26.8°C at atmospheric pressure). The industrial method of manufacture of this compound consists of the interaction of an alcoholic solution of 1,1,2-trichlorotrifluoroethane (Freon-113) with zinc, which is preliminarily activated with hydrochloric acid:



The yield of the product is close to theoretical, but the excessive consumption of zinc invoked the search for other ways of chlorine elimination. It has been reported that the action of hydrogen in the presence of hydrogenation catalysts (Cu, Co) makes it possible to eliminate chlorine and to obtain $\text{CClF}=\text{CF}_2$ in high yield (77-96 percent):



Monochlorotrifluoroethylene is polymerized in the presence of initiators that are used for radical-chain reactions to polychlorotrifluoroethylene (Fluoroplast-3):



In terms of chemical inertness this polymer is close to polytetrafluoroethylene, but it is inferior in thermal stability. It has good dielectric properties and is readily shaped into finished articles by conventional moulding and pressure casting methods; it is suitable for applying protective coatings.

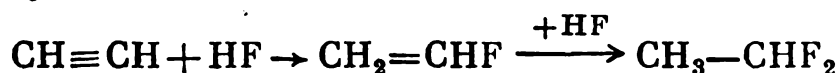
The thermal degradation of polychlorotrifluoroethylene gives liquid products, which have lubricating properties. It is even better to produce these liquid compounds by telomerization of monochlorotrifluoroethylene with halogen derivatives (chloroform, carbon tetrachloride) in the presence of initiators:



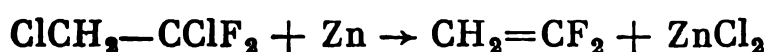
In order to replace the remaining hydrogen atoms, the oil is treated with cobaltic trifluoride and distilled into fractions of differing viscosity. In lubricating properties, chemical and thermal stability these fractions are similar to fluorocarbons and are used for the same purposes.

Other important fluoro-organic monomers are vinyl fluoride, vinylidene fluoride and hexafluoropropylene.

Vinyl fluoride, $\text{CH}_2=\text{CHF}$, is produced by addition of hydrogen fluoride to acetylene in the presence of catalysts, such as antimony and barium chloride supported on activated charcoal. The by-product formed is ethylidene fluoride:

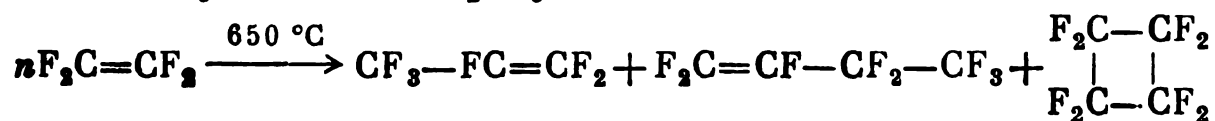


Vinylidene fluoride, $\text{CH}_2=\text{CF}_2$, is obtained by the dechlorination of 1,1-difluoro-1,2-dichloroethane in the presence of zinc:



It is used for the production of important fluorinated rubbers, which possess high thermal and chemical stability. For this purpose, vinylidene fluoride is copolymerized with tetrafluoroethylene, perfluoropropylene or monochlorotrifluoroethylene.

Hexafluoropropylene (perfluoropropylene) is formed together with perfluoro-*n*-butylene and perfluorocyclobutane upon pyrolysis of tetrafluoroethylene or its polymer:



CHAPTER 3

HYDROLYSIS, HYDRATION, DEHYDRATION, ESTERIFICATION AND AMIDATION

All these processes are very important in the industry of basic organic and petrochemical synthesis. The hydrolysis of fats, cellulose and carbohydrates has long been used for the manufacture of soap, glycerine, ethyl alcohol and other valuable products. In the field of organic synthesis the processes under consideration are employed mainly for the production of C_2 - C_6 alcohols, phenols, ethers, α -oxides, many unsaturated compounds, carboxylic acids and their derivatives (esters, anhydrides, nitriles, amides) and other compounds.

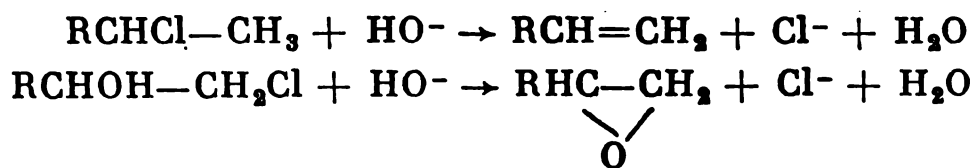
The compounds indicated above are of great practical importance as intermediates in organic synthesis (alcohols, acids and their derivatives, aldehydes, α -oxides), monomers and feedstock for the synthesis of polymeric materials (phenol, esters of acrylic and methacrylic acids, melamine, chloro-olefins), plasticizers and lubricants (esters), solvents (alcohols, ethers, esters, chloro-olefins), pesticides (esters of carbamic and thiocarbamic acids). The reactions that are very often referred to in this chapter constitute an intermediate stage in multistep syntheses of other major products.

The compounds mentioned above are produced on a large scale. For example, in the United States, the forecast for 1980 was about 900,000 tons of ethyl and isopropyl alcohols, about 1,000,000 tons of propylene oxide, 250,000 tons of epichlorohydrin, more than 2,000,000 tons of esters, and about 300,000 tons of isocyanates.

Classification and Brief Survey of Reactions. Hydrolysis is the term used for reactions involving a replacement or double exchange that occurs through the agency of water or alkalis. These reactions may be classified as hydrolysis reactions that proceed with the cleavage of carbon-chlorine, carbon-oxygen, carbon-nitrogen, etc., bonds. For chloro derivatives, apart from the hydrolysis with replacement of chlorine



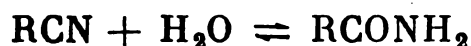
there may also take place the alkaline dehydrochlorination with the formation of unsaturated compounds or α -oxides:



In contrast to hydrolysis, *hydration* reactions involve the addition of water across unsaturated carbon-carbon bonds:



across triple carbon-nitrogen bonds of nitriles, etc.:

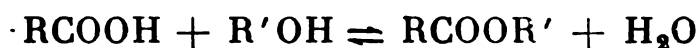


Some hydration reactions are at equilibrium; the reverse process of water elimination are called *dehydration*, which may be either intra- or intermolecular:



The liberation of water occurs in many organic reactions (esterification, nitration, etc.), which is why the term dehydration is applied only to those processes which are not classified by any other system.

Close to hydrolysis, hydration and dehydration are *esterification* reactions, whose reverse direction is the hydrolysis of esters:



In turn, esterification reactions are analogous to *amidation* reactions, which consist of the synthesis of acid amides; the reverse direction is the hydrolysis of amides to acids:



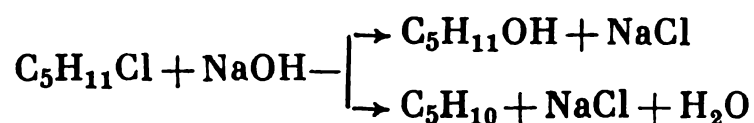
Combinations of the reactions described above are also employed. Examples of such combined processes are: hydrolysis and esterification; dehydration and esterification; amidation and dehydrochlorination; amidation and esterification. For this reason, these reactions are all described in this chapter.

3.1. Hydrolysis and Alkaline Dehydrochlorination of Chloro Derivatives

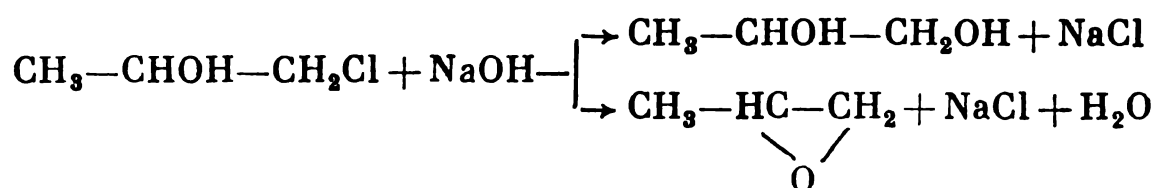
Chloro derivatives are often used as intermediates with the purpose of their further conversion by way of hydrolysis and alkaline dehydrochlorination. First, a chlorine atom, which is usually highly mobile, is introduced into the starting hydrocarbon, and then the chloro derivative is subjected to the action of hydrolyzing agents. In this way certain alcohols, phenols, chloro-olefins and α -oxides are produced on a commercial scale.

3.1.1. Chemistry and Theoretical Foundations of the Hydrolysis of Chloro Derivatives

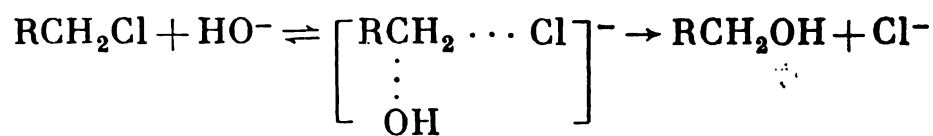
The hydrolysis of chloro derivatives through the agency of water proceeds as a slow reversible reaction, which is why aqueous solutions of stronger hydrolyzing agents are used for carrying out the process: NaOH, Ca(OH)₂ or Na₂CO₃. The action of these agents makes the reaction irreversible. In a general case, both the replacement of a chlorine atom by a hydroxyl group, which is a classical example of hydrolysis, and the alkaline dehydrochlorination are possible:



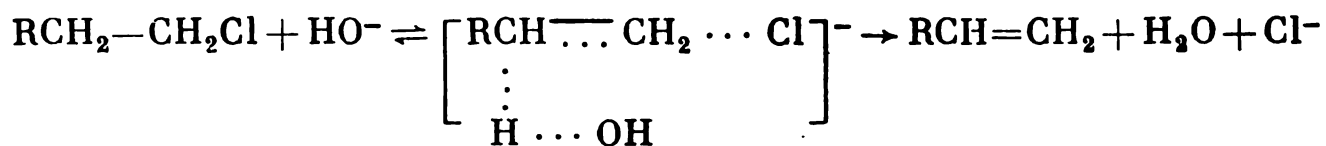
When chlorohydrins are acted on by alkalis, either substitution or elimination is possible with the formation of glycols and α -oxides:



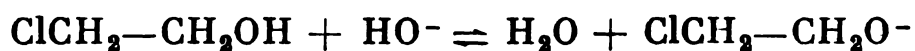
Reaction Mechanism and Kinetics. The hydrolysis and alkaline dehydrochlorination of chloro derivatives are nucleophilic substitution and elimination reactions. In the majority of practically important cases they proceed by a bimolecular mechanism. The rate-limiting step in hydrolysis is the attack of the hydrolyzing agent on a carbon atom bearing a chlorine atom, a new bond being formed at the same time as the old one is broken (the S_N2 mechanism):



Upon elimination of HCl the attack of the hydroxyl ion is directed to the hydrogen atom attached to the β -carbon atom (the E2 mechanism):

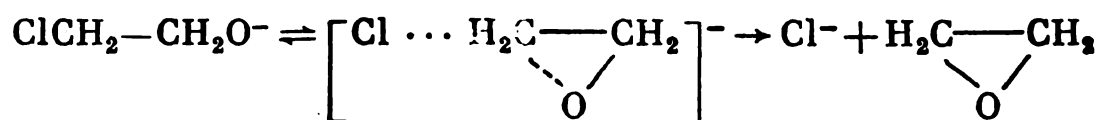


In an analogous reaction with chlorohydrins an acid-base equilibrium is rapidly set up:

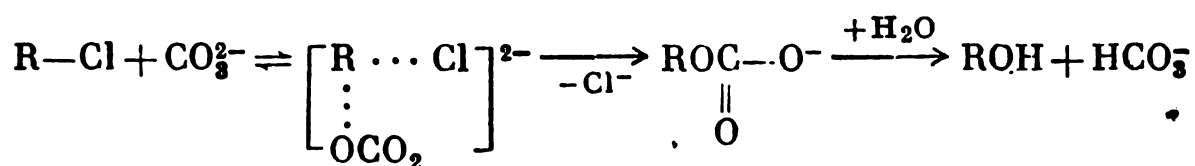


and the alkoxide ion formed undergoes intramolecular ring closure accompanied by the weakening of the old bond and the formation

of a new one:



Upon hydrolysis by an aqueous solution of soda the process is partly effected by hydroxyl ions resulting from the water hydrolysis of soda, but the CO_3^{2-} and HCO_3^- ions also take part in it. The mechanism of hydrolysis by these ions consists of the intermediate formation of unstable carbonates, which decompose into alcohols:



All these mechanisms are first order with respect to both reactants under homogeneous hydrolysis conditions and the overall reaction order is 2. In the presence of various hydrolyzing agents in the solution we have the following kinetic equation:

$$r = (k_0 + k_{\text{HO}^-} [\text{HO}^-] + k_{\text{CO}_3^{2-}} [\text{CO}_3^{2-}] + k_{\text{HCO}_3^-} [\text{HCO}_3^-]) [\text{RCl}]$$

where k_0 , k_{HO^-} , $k_{\text{CO}_3^{2-}}$, and $k_{\text{HCO}_3^-}$ are the hydrolysis constants for hydrolysis reactions effected by water, and hydroxyl, carbonate and bicarbonate ions. The reaction, however, is homogeneous only with chlorohydrins, whereas most chloro derivatives are sparingly soluble in water and the process occurs in a heterophase medium. The reaction proceeds in a water-alkaline phase and is speeded up by intensive mixing of the stream, which removes diffusional retardation when RCl passes from the organic to the aqueous phase. The reaction rate will then be described by the above kinetic equation with [RCl] representing the concentration of the chloro derivative in the aqueous phase determined by the distribution coefficient. If the products are not present in the organic phase, [RCl] is practically a constant quantity determined by the solubility of the chloro derivative, and the reaction velocity will depend only on the concentration of the hydrolyzing agents. But if the products pass into the organic phase, thereby diluting the chloro derivative, its concentration in water will fall off as the reaction is progressing, as a result of which the reaction velocity will decrease with conversion of the chloro derivative. In the latter case, the kinetic description of the process becomes complicated.

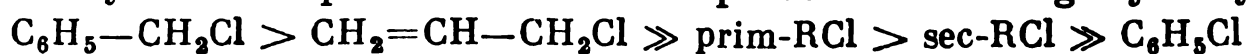
So-called *phase-transfer catalysts* have been lately proposed for such reactions. These catalysts are tetra-substituted ammonium salts or bases, in which one of the alkyl groups is sufficiently long to render them soluble not only in the aqueous but also in the organic phase.

The base $\text{R}(\text{CH}_3)_3\text{N}^+\text{OH}^-$ passes over into the organic phase and effects

the hydrolysis of the chloro derivative, being itself converted to the salt $R(CH_3)_3\overset{+}{N}\overset{-}{Cl}$. This salt returns into the aqueous phase, and under the action of the alkali there again is formed a base, which repeats the above-described cycle of phase transitions and reactions.

It has been suggested that surfactants be also added in some cases in order to accelerate the process; surfactants will emulsify the mixture and contribute to the removal of diffusional retardation.

In accordance with the reaction mechanism considered above, the chloro derivatives may be arranged in the following order of reactivity with respect to chlorine replacement during hydrolysis:



This order depends on the magnitude of the partially positive charge on the carbon atom bearing a chlorine atom. In alkaline dehydrochlorination the reactivity increases with increasing acidity of the hydrogen atom attached to the β -carbon atom. This is usually favoured by the presence of electron-withdrawing substituents, including halogen atoms.

Selectivity of the Process and Its Control. As shown above, when chloro derivatives are acted on by alkalis, substitution and HCl elimination reactions may occur concurrently, only one of these reactions leading to the end product. The extent of these reactions is influenced by temperature, the properties of the medium and by other factors, but

in practice the most efficient means of controlling the direction of these reactions is the choice of the hydrolyzing agent. We have already seen that upon substitution the hydrolyzing agent, while attacking the carbon atom, displays its nucleophilic properties, whereas upon elimination, attaching itself to a hydrogen atom, it behaves as a base. Hence, substitution reactions require a weak base of relatively high nucleophilicity (say Na_2CO_3), and for the elimination of HCl a strong base is needed with relatively low nucleophilicity, say NaOH or $Ca(OH)_2$. This dependence of the process selectivity on the type of hydrolyzing agent and the pH of the medium is shown in Fig. 3.1.

The alkaline dehydrochlorination of chloro derivatives may also involve a different system of parallel reactions, with the hydrogen being eliminated from different carbon atoms, this leading to the

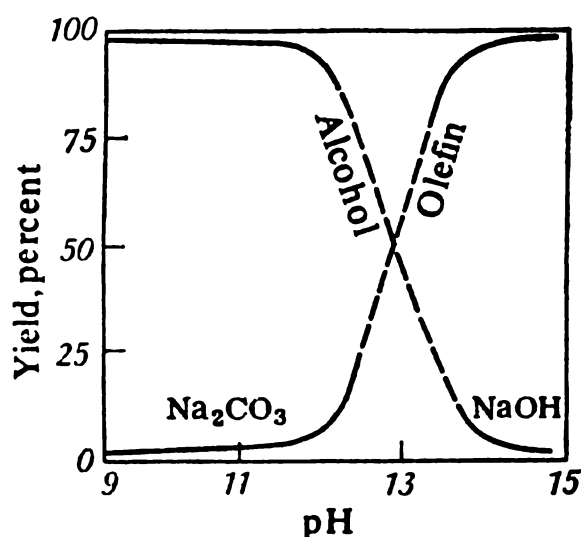
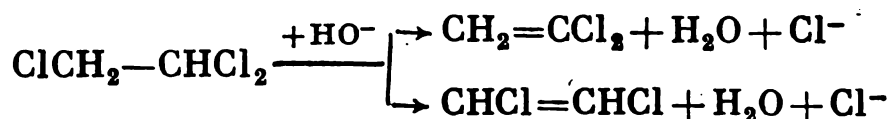


Fig. 3.1. Dependence of the yield of substitution and elimination products upon treatment of chloropentanes with water solutions of alkalis on the pH of the medium.

formation of isomeric olefins or chloro-olefins; one example is

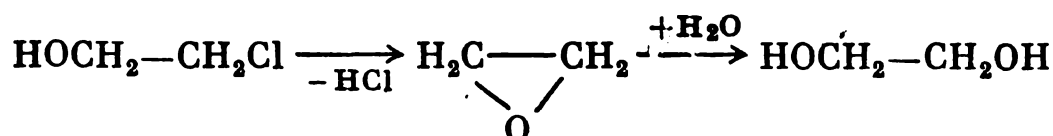


The predominant direction of the reaction is determined by the Zaitsev rule. In this respect, alkaline dehydrochlorination is more selective than thermal dehydrochlorination, and is therefore chosen for the synthesis of certain chloro-olefins.

Of importance are the successive paths of by-product formation. Upon HCl elimination the extent of dehydrochlorination may be such that acetylene derivatives are formed:

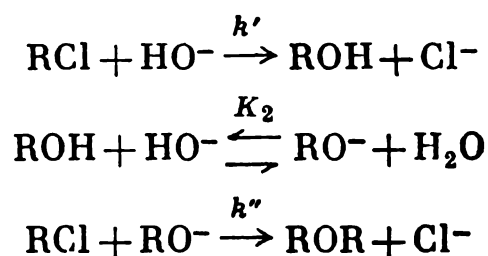


or the hydrolysis of α -oxides to glycols may occur:



The most effective way of suppressing these side reactions is to reduce the concentration of the end product in the reaction mass by way of its continuous distillation. This is favoured by the fact that the end product is always more volatile than the reactants, and not infrequently it forms with water an even lower-boiling azeotropic mixture.

In hydrolysis by water the by-product of successive conversions is an ether. The formation of an ether is accounted for by the fact that the primary reaction product, an alcohol, enters into a rapid acid-base exchange reaction with alkali to give an alkoxide, which is also capable of interaction with a chloro derivative:



In accordance with this mechanism, the differential selectivity with respect to alcohol, the hydrolysis by water being neglected, is given by

$$\varphi_{\text{ROH}} = \frac{d[\text{ROH}]}{d[\text{RCl}]} = 1 - \frac{k''K_2}{k'} \cdot \frac{[\text{ROH}]}{[\text{H}_2\text{O}]}$$

Thus, the selectivity must decrease as the alcohol is accumulated in the reaction mass or, in other words, with increasing ratio of the chloro derivative to water taken for the reaction (see Fig. 3.2). When hydrolysis is effected by strong bases, the selectivity is strongly lowered, since the alkoxides are more reactive than the hydroxyl

on ($k'' > k'$), and, in spite of the position of the equilibrium of the condensation reaction, the product (k''/K_2) k' is usually larger than unity.

In hydrolysis effected by sodium carbonate, in accordance with the mechanism described above, the reaction with the carbonate ion gives only an alcohol and an ether can be obtained only as a result of the reaction with alcohol or with an alkoxide formed from the hydroxyl ion—the product of the hydrolysis of sodium carbonate in water. The differential selectivity will then be given by

$$\begin{aligned} \varphi_{\text{ROH}} &= \frac{d[\text{ROH}]}{d[\text{RCl}]} = \\ &= 1 - \frac{\left(k_0'' + k_{\text{RO}}'' - K_2 \frac{[\text{HO}^-]}{[\text{H}_2\text{O}]} \right) [\text{ROH}]}{k_0' + k_{\text{HO}^-}' [\text{HO}^-] + k_{\text{CO}_3^{2-}}' [\text{CO}_3^{2-}] + k_{\text{HCO}_3^-}' [\text{HCO}_3^-]} \end{aligned}$$

where k_0 are the rate constants of the reactions with water and alcohol; k_i' and k_i'' are the rate constants of the formation of an alcohol and an ether. A comparison of the two equations given above shows that in the latter case the selectivity must be higher and also dependent on the molar ratio of the chloro derivative to water (Fig. 3.2, curve 1).

Thus, hydrolysis with the replacement of a halogen atom should be carried out using sodium carbonate, since this prevents HCl elimination and reduces the side formation of an ether. The optimal ratio of the chloro derivative to water is chosen on the basis of economic considerations, by comparing the selectivity with energy consumption for the distillation of excess water (usually, this optimum corresponds to the preparation of aqueous solutions of alcohol with concentration of 1-1.5 mole/litre). Finally, in order to raise the selectivity of hydrolysis it is expedient to use reactors that are close in design to the plug-flow model.

In contrast to what has been said above, the hydrolysis of aryl chlorides is effected using not sodium carbonate but a more reactive aqueous solution of sodium hydroxide because of the low reactivity of aryl chlorides and also because the HCl elimination is impossible. In such a case, the side formation of an ether is not so important, since at a high reaction temperature diaryl ether is hydrolyzed by

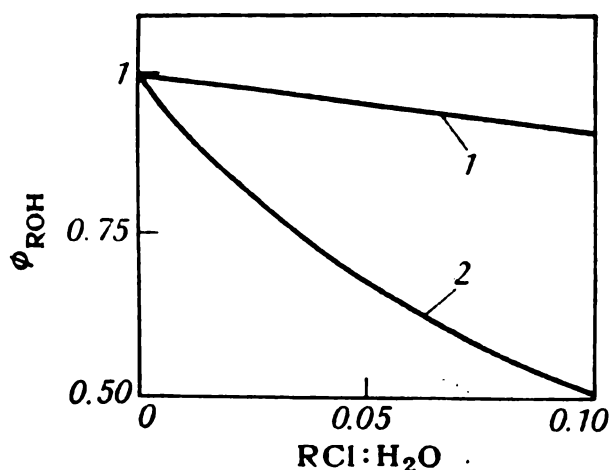


Fig. 3.2. Dependence of the selectivity of the reaction with respect to allyl alcohol on the molar ratio of allyl chloride to water upon hydrolysis by sodium carbonate (1) and sodium hydroxide (2).

water and can be returned to the reaction:

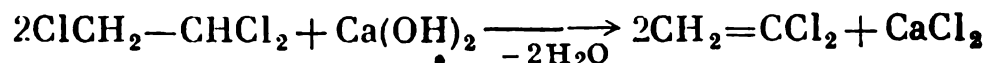


The hydrolysis of aryl chlorides requires a double amount of alkali because the end product is a phenolate (phenate) rather than a phenol

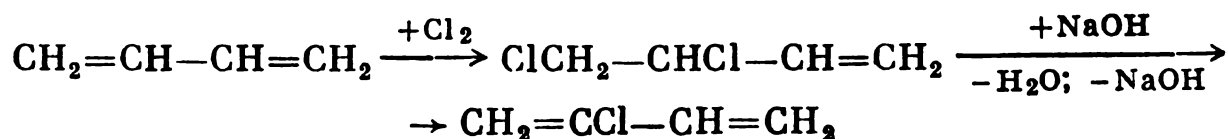
3.1.2. Production of Chloro-Olefins and α -Oxides by Alkaline Dehydrochlorination

Two principal types of this process involve the formation of chloro-olefins and α -oxides. Both processes were the basis for the first industrial methods of manufacture of these products, but since then their importance has gradually declined. It is because other, more efficient methods of synthesis were developed, which involved neither the consumption of extra chlorine and alkali nor the increased formation of waste waters and salts.

Chloro-Olefins Produced by Alkaline Dehydrochlorination. The competition to this method comes from the thermal dehydrochlorination (see Chapter 2) accompanied by chlorination or oxidative chlorination. As a result, alkaline dehydrochlorination is not employed at present for the production of vinyl chloride (from 1,2-dichloroethane) and is not promising for the manufacture of trichloroethylene (from tetrachloroethane) and tetrachloroethylene (from pentachloroethane). Still, it remains to be of value for the production of vinylidene chloride from 1,1,2-trichloroethane owing to its high selectivity (with respect to the direction of HCl elimination according to the Zaitsev rule):



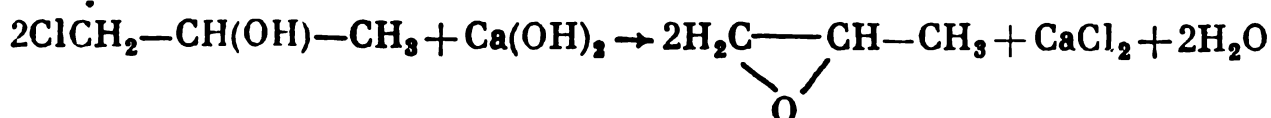
and for the production of chloroprene by a new route of its synthesis via 1,3-butadiene and 1,2-dichloro-3-butene:



The properties, applications and other methods of manufacture of these products have already been described (see Sections 2.3.2.2. and 2.4.1).

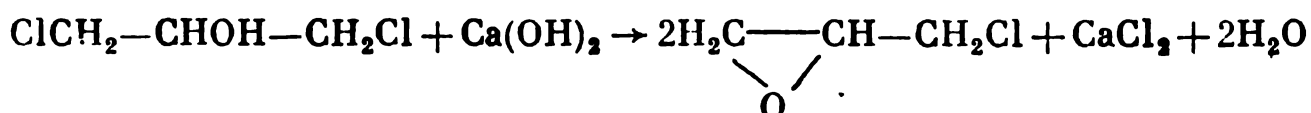
α -Oxides Produced by Alkaline Dehydrochlorination. The competition to the chlorine method of synthesis comes from oxidation processes. As a result, alkaline dehydrochlorination of chlorohydrins is not employed today for the production of ethylene oxide, but the

major proportion of propylene oxide is still made by this process:

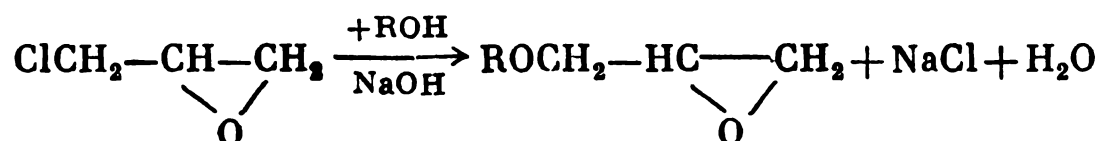


Propylene oxide (a liquid, b.p. 33.9 °C) is produced on a large scale and is used for the manufacture of propylene glycol ($\text{OCH}_2\text{—CHOH—CH}_3$), polypropylene glycols and nonionic surfactants and also as a pesticide (say, for food preservation).

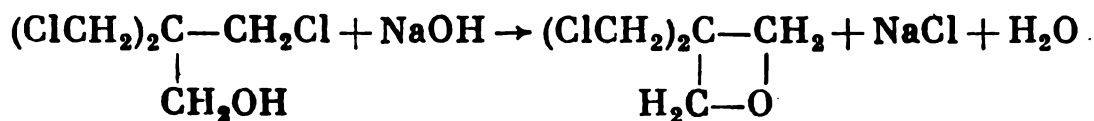
Epichlorohydrin (a liquid, b.p. 117 °C) is a further important product made by alkaline dehydrochlorination of glycerol dichlorohydrin:



Epichlorohydrin is mainly used for the production of epoxide polymers (the products of its polycondensation with bisphenols). These polymers are noted for their high adhesive capacity and thermal stability, which makes them especially suited for the manufacture of coatings, fibre-glass plastics, etc. Besides, epichlorohydrin is the starting stock for the production of synthetic glycerol, glycidyl alcohol and its esters



Bis(chloromethyl) oxacyclobutane is a new interesting monomer obtained by alkaline dehydrochlorination of pentaerythritol trichlorohydrin with closure of the four-membered oxide ring:



1.2.1. Technology of Alkaline Dehydrochlorination

As follows from what has been said above, alkaline dehydrochlorination is carried out using aqueous solutions of strong alkalis [use is most often made of Ca(OH)_2 , which is cheaper, but NaOH is also occasionally used] with continuous distillation of the end product from the reaction mass. The elimination of HCl occurs most readily in chlorohydrins; it is more difficult with ethane polychlorides, but the process is always conducted at atmospheric pressure and at a temperature of 100 °C, which provides the boiling of the mixture and the distillation of the product.

The flow diagram of epichlorohydrin production is shown in Fig. 3.3. Aqueous solutions of Ca(OH)_2 and glycerine dichlorohydrin

are fed into reaction column 1 and live steam is introduced into the pipe still; this steam is used for the heating and distillation of the products. At the trays there takes place a dehydrochlorination reaction with the formation of epichlorohydrin and by-product glycerine. The latter flows down into the column still, from which the aqueous solution of CaCl_2 and excess caustic are withdrawn for purification. The volatile products together with steam are condensed in cooler condenser 2 and the condensate is separated in separator 3 into two

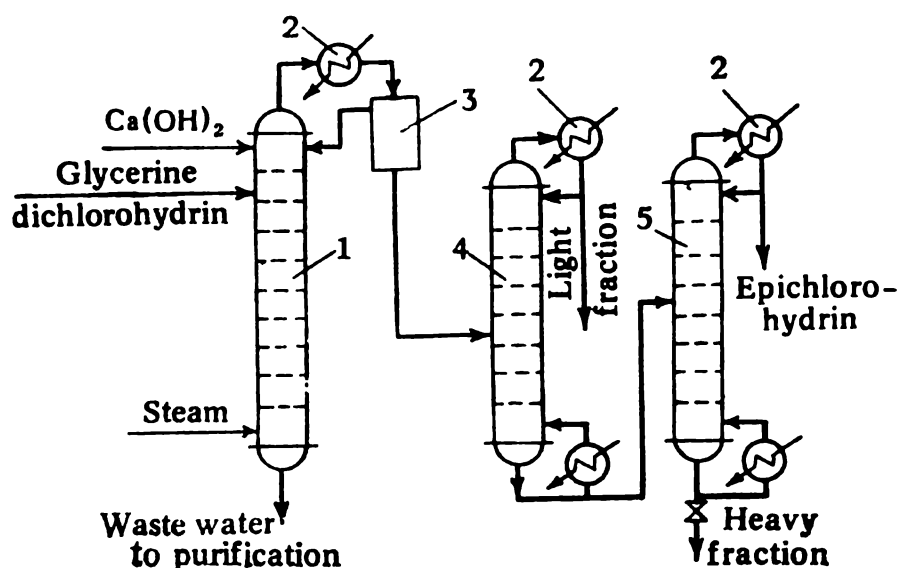


Fig. 3.3. Flow diagram of epichlorohydrin production:

1—reactor; 2—cooler-condenser; 3—separator; 4—column for distillation of the light fraction; 5—column for separation of the heavy fraction.

phases: an aqueous phase containing 6 percent of dissolved epichlorohydrin and an organic phase containing 85-90 percent of epichlorohydrin (with water, trichloropropane, unconverted glycerine dichlorohydrin and volatile substances, such as allyl chloride and 2,3-dichloropropylene present as impurities). The aqueous phase is returned to reflux reactor 1 and the organic phase is withdrawn for separation.

First, in column 4 the water is distilled off together with the volatile substances, which are the process wastes. The still liquid passes from this column for distillation to column 5, where the epichlorohydrin is distilled off from the heavier products accumulated in the still. This mixture of unconverted chlorohydrin and trichloropropane is additionally separated, the chlorohydrin being returned to hydrolysis and the trichloropropane removed from the system as a commercial product (it is expedient to process it to tetrachloroethylene and CCl_4 by chlorinolysis). The epichlorohydrin taken from the top of column 5 has a purity of 98-99 percent; it is additionally purified to a 99.5-percent concentration by fractionation (not shown in the flow diagram).

In alkaline dehydrochlorination involving the formation of chloroolefins the reaction unit is of the same design as the preceding one.

When propylene oxide completely miscible with water is to be produced, partial condensation of the vapours is effected in cooler 2 and separator 3 is used to separate the condensate from the vapours. The condensate is returned to reflux reactor 1, and the vapours, which consists mainly of propylene oxide, are sent for fractionation.

1.3. Production of Alcohols and Phenols by Hydrolysis

From what has been said above it is clear that the hydrolysis of chloro derivatives involving the replacement of chlorine atoms is effected in excess water using sodium carbonate (production of alcohols) or sodium hydroxide (production of phenols). Depending on the reactivity of chloro derivatives, the process is carried out at 0-125 °C (hydrolysis of allyl chloride) and 300-350 °C (hydrolysis of chlorobenzene). Evidently, in order to keep the mixture in the liquid state the pressure must range from 0.5-1 to 10 MPa. Under these conditions the contact time varies from a few minutes to 1-30 min.

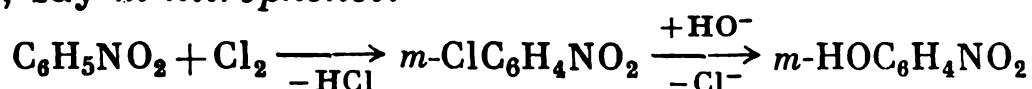
This chlorine method of manufacture of alcohols and phenols was formerly extensively used, but today it has lost its importance because of the development of more economical methods which do not require the consumption of chlorine and alkalis and do not involve the formation of a large amount of waste waters. For example, phenol was produced from chlorobenzene:



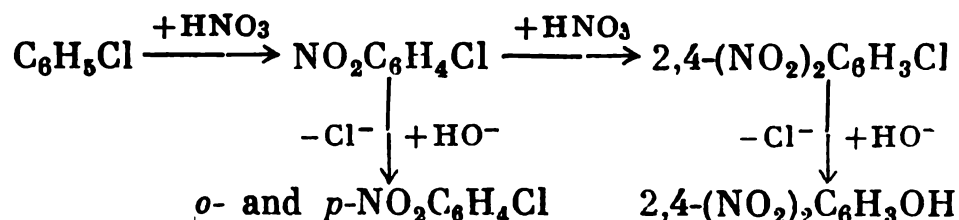
In the modified method, benzene is subjected to oxidative chlorination followed by the gas-phase hydrolysis of chlorobenzene using HCl at the oxychlorination stage (the Raschig process):



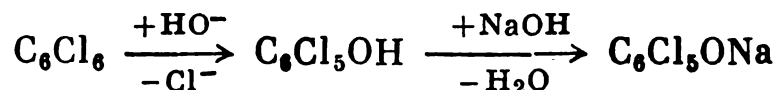
As a result, chlorine is not consumed at all, and the overall process reduces to the oxidation of benzene to a phenol. In spite of the improvement, the chlorine methods of phenol production are gradually abandoned, but they are used for the synthesis of some phenol derivatives, say *m*-nitrophenol:



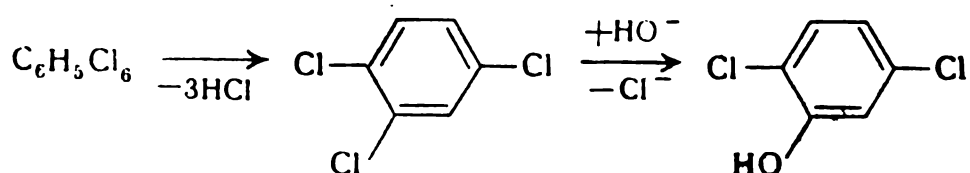
- and *p*-nitrophenols and 2,4-dinitrophenols:



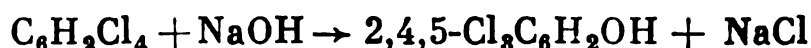
Basic hydrolysis is also employed to produce many chlorophenols. For instance, hexachlorobenzene is the feedstock for the synthesis of the above-mentioned pesticides *pentachlorophenol* and *sodium pentachlorophenate*:



The production of *dichlorophenols* developed on the basis of the inactive components of hexachlorocyclohexane isolated from it upon concentration of the γ -isomer (see Sec. 2.2.2.2). For this purpose, hexachlorane is subjected to thermal dehydrochlorination and the 1,2,4-trichlorobenzene formed to basic hydrolysis:



In an analogous way, *2,4,5-trichlorophenol* is obtained from 1,2,4,5-tetrachlorobenzene:

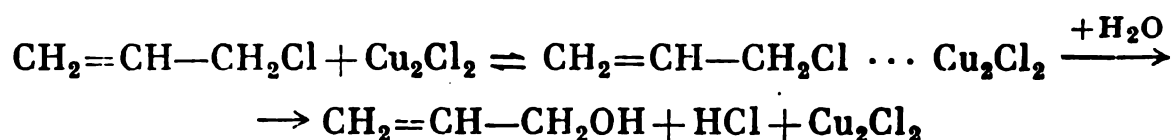


and 2,4,5-trichlorophenol goes to the production of copper trichlorophenate and sodium trichlorophenoxyacetate, which are well-known as pesticides.

The basic hydrolysis of chloro derivatives is still of some value for the production of alcohols, namely as the route for the synthesis of *allyl alcohol*:

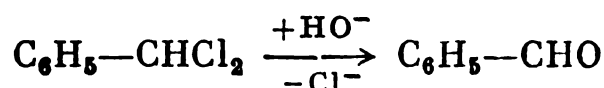


Allyl alcohol (a liquid, b.p. 96.2 °C) is used for the production of allyl esters of phthalic, phosphoric, and other acids (these esters are monomers); it serves as an intermediate in one of the methods of synthesis of glycerol. Apart from the basic hydrolysis of allyl chloride, allyl alcohol can also be obtained by water hydrolysis in the presence of a catalyst (cuprous chloride in a hydrochloric acid medium). The method is suitable only for reactive chloro derivatives of the allyl type, when the activation of the molecule due to the formation of a complex with Cu_2Cl_2 is sufficient for substitution:

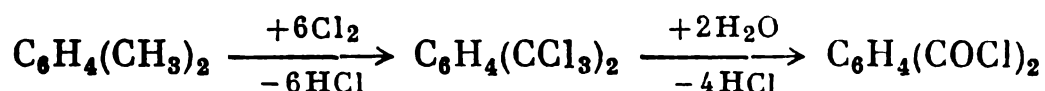


The hydrolysis is carried out using a 0.2-percent solution of Cu_2Cl_2 in 2-2.5-percent hydrochloric acid at 80 °C. The by-products formed are diallyl ether and propionaldehyde.

The hydrolysis of *gem*-dichloro derivatives gives aldehydes, the process being employed on a commercial scale for the manufacture of *benzaldehyde* from *benzal chloride*:

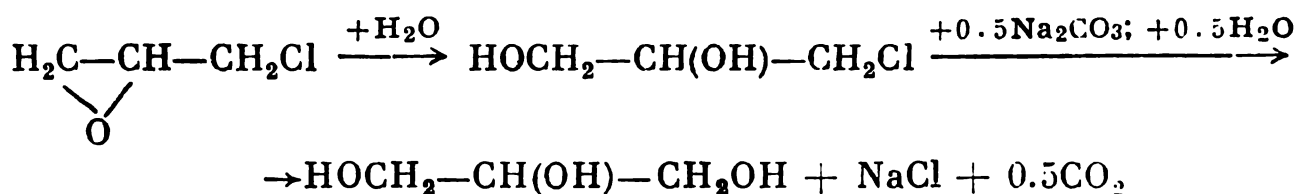


gem-Trichloro derivatives when subjected to hydrolysis give carboxylic acids, which are formed via the intermediate step of formation of acid chlorides. The latter have low reactivity for aromatic acids and may only be the major products of the hydrolysis of chloromethyl derivatives of benzene. In this way, *acid chlorides* *iso*- and *terephthalic acids* are made from *m*- and *p*-hexachloroxyls:

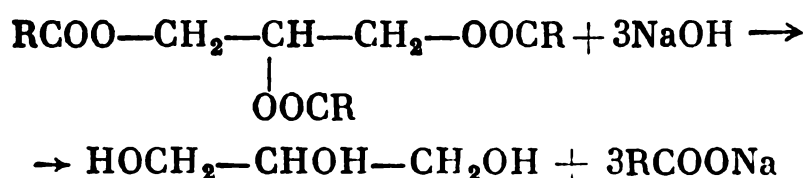


which are used for the synthesis of heat-resistant polymers. The hydrolysis is carried out batchwise at 80–100 °C, and a stoichiometric amount of water is gradually added on mixing to the hexachloride containing a small amount of catalyst (FeCl_3).

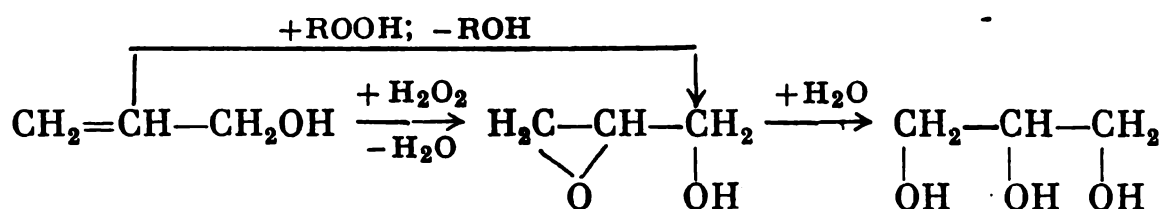
A complicated but industrially important example of the processes under consideration is the hydrolysis of epichlorohydrin. This compound contains a halogen atom and a three-membered epoxide ring. The latter is hydrolyzed by water in the presence of a catalyst (Na_2CO_3), following which the chlorine atom is replaced to give glycerol:



The by-products formed in this process are the ethers of glycerol. *Glycerine* (*glycerol*) is a colourless viscous syrup of sweet taste (b.p. 290 °C). It is widely used for the production of glyphthalic polymers—the products of its polycondensation with phthalic anhydride, and also for the manufacture of nitroglycerine powders, the solvent triacetine (glycerol triacetate) and also of cosmetic and medicinal preparations. Glycerol occurs in nature in the form of esters of various animal fats and vegetable oils. The hydrolysis (saponification) of the latter gives glycerol and soap simultaneously and was the first method of manufacture of glycerol. Glycerol is still mainly produced by this method:



The first method of producing synthetic glycerine from propylene via allyl chloride, glycerine dichlorohydrin and epichlorohydrin was employed on an industrial scale in 1948. This chlorine method of glycerine synthesis is still used at present despite its shortcomings (the consumption of chlorine and caustic, the formation of waste waters) because the synthesis via allyl alcohol



proved even less economical.

3.1.3.1. Technology of Alkaline Hydrolysis

The hydrolyzing agent used is a 5- to 10-percent solution of Na_2CO_3 or NaOH , which is taken in an excess of 10-25 percent with respect to the stoichiometric amount in order to provide a higher intensity of the process and to increase the degree of conversion of a chlorine derivative. Since two liquid phases are present, an increase in their interface becomes important. In continuous processes this is usually achieved in the pump, into the suction line of which are fed the two reagents. The system is maintained in the emulsified state by agitation of the stream due to its high linear velocity. This calls for the use of coil or multichannel shell-and-tube reactors, which is possible with a short reaction time. When the reaction time is long and the product is made on a small scale, the process is operated batchwise in an autoclave; the mixture is stirred by a mixer or steam of the appropriate pressure is bubbled through the mixture.

Upon completion of the process the reaction mass is throttled to atmospheric pressure, the end product being passed into the gas phase (allyl alcohol) or left in the liquid phase (glycerol, phenol in the form of phenates). The volatile alcohols are then isolated by fractionation. When glycerol is to be produced, all of the water has to be distilled off with simultaneous separation of NaCl ; when phenols are the end products, the aqueous phase is acidified and the phenols formed are crystallized. We shall now describe this process for the production of synthetic glycerol by the chlorine method.

Synthesis of Glycerol from Epichlorohydrin (Fig. 3.4). Epichlorohydrin and a 5- to 6-percent soda solution are emulsified in pump 1, in which the mixture is compressed to 0.6-1 MPa and pumped through preheater 2 into tubular reactor 3. The above-described reactions are carried out in reactor 3 with the formation of glycerol and its ethers. The reaction mass is throttled in valve 4 to atmospheric pressure, and the gas-vapour phase (CO_2 and water vapours) is separated in separator 5 from the liquid phase (aqueous solutions).

glycerol, its ethers, NaCl and unconverted Na_2CO_3). In view of the large difference in volatility between water and glycerol, the major proportion of water is separated by evaporation: the liquid passes successively through a series of stripping stills 6; the first of these is heated by externally supplied steam and the second, which

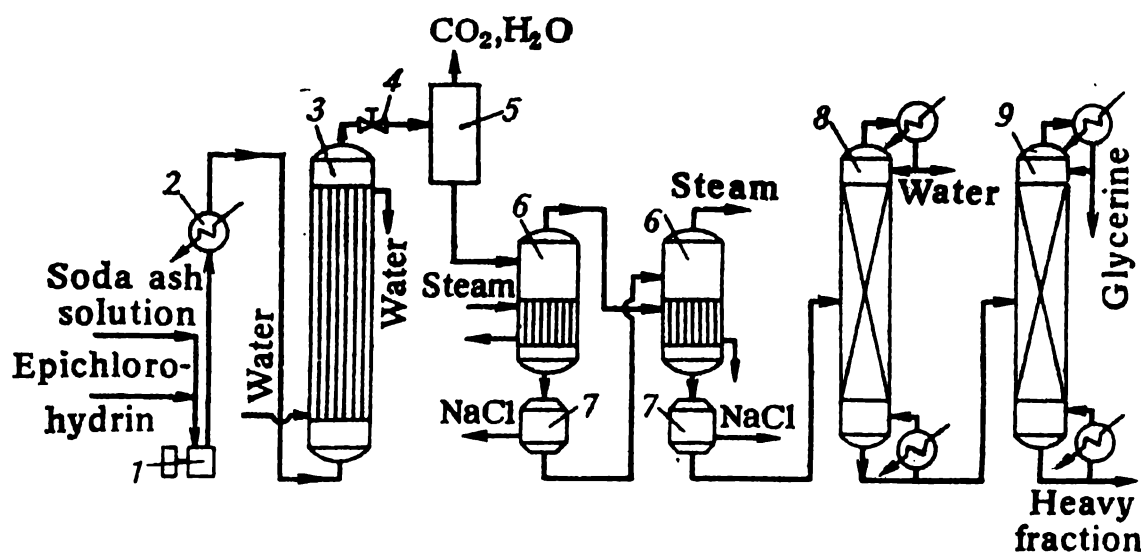


Fig. 3.4. Flow diagram of glycerine production by the chlorine method: 1—pump; 2—preheater; 3—reactor; 4—throttle valve; 5—separator; 6—stripping stills; 7—filters; 8—water separation column; 9—column for separation of the heavy fraction.

operates in a vacuum, is heated by the steam from the first still. The liquid leaving each of the strippers passes through filters 7, where it is separated from the NaCl.

After the evaporation the nearly 80-percent glycerol is subjected to vacuum fractionation in column 8 in order to remove the water and in column 9 to remove the high-boiling glycerol ethers left in the still. The distillate from the last column is glycerol of 98 to 99 percent purity. It is often subjected to additional purification (coloration), the coloured impurities being adsorbed by activated charcoal.

2. Hydration and Dehydration Processes

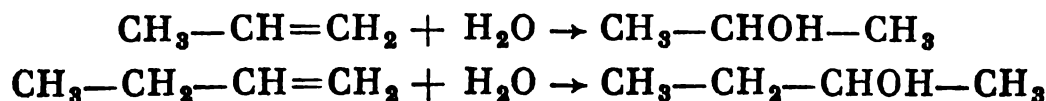
These processes are employed on a large scale to produce various compounds, especially lower alcohols and numerous unsaturated compounds.

1. Chemistry and Theoretical Foundations of the Process

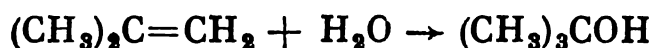
The addition of water to olefins occurs according to the Markovnikov rule; as a result, ethanol is formed from ethylene:



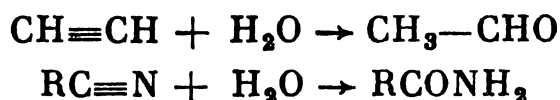
and isopropyl and *sec*-butyl alcohols are formed from propylene and *n*-butylene, respectively:



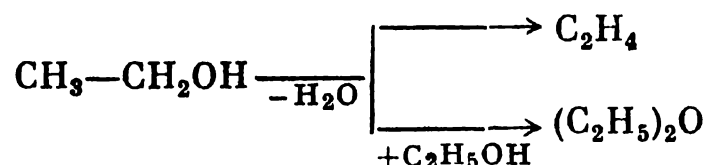
and isobutylene gives *tert*-butyl alcohol:



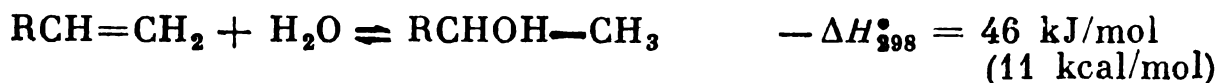
Hydration across the triple bonds of acetylene and nitriles gives carbonyl compounds—acetaldehyde and an amide:



These conversions are all reversible, but the elimination of water from alcohols (and from hydroxyl-containing compounds in general) can occur in two directions: both as an intra- or an intermolecular reaction:



Thermodynamics of the Reactions. We shall consider the equilibrium of the basic reaction: hydration and intramolecular dehydration:



It proceeds with evolution of heat and, hence, its equilibrium is shifted to the right with decreasing temperature. On the contrary dehydration is favoured by heating. The free energy change upon hydration of ethylene, propylene and isobutylene as a function of temperature is shown in Fig. 3.5. It can be seen that the equilibrium is unfavourable for the hydration of olefins because at 150–300 °C when the catalysts used are sufficiently active, ΔG° has a large positive value and the equilibrium is displaced to the side of dehydration. For olefins of different structure the differences in the thermodynamics of the reactions under consideration are insignificant.

As is shown by the stoichiometry of the reactions, their equilibrium can be influenced by changing the pressure. The intramolecular dehydration, which involves an increase in the number of moles of the substances, is favoured by a lowered or ordinary pressure. On the contrary, the hydration of olefins is favoured by a high pressure which increases the equilibrium degree of conversion of olefins. For instance, the equilibrium degree of conversion at 250–300 °C and atmospheric pressure is only 0.1–0.2 percent, which is absolutely unsuitable for practical purposes, but at 7–8 MPa and the same tem-

peratures it reaches 12-20 percent. The dependence of the equilibrium degree of conversion of ethylene upon its hydration on pressure and temperature is shown in Fig. 3.6; analogous curves are characteristic of other olefins as well. It is evident that hydration is favoured by a simultaneous decrease in temperature and increase in pressure.

Let us now consider the equilibrium in the process involving the intermolecular dehydration of alcohols and the hydrolysis of ethers:



With ethanol the equilibrium of the process is described by the following equation:

$$\log K_p = -1.40 + \frac{1200}{T}$$

which shows that it is shifted to the right with decreasing temperature. Hence, at 200-400 °C the intra- and intermolecular dehydrations compete with each other. The directions of these reactions can

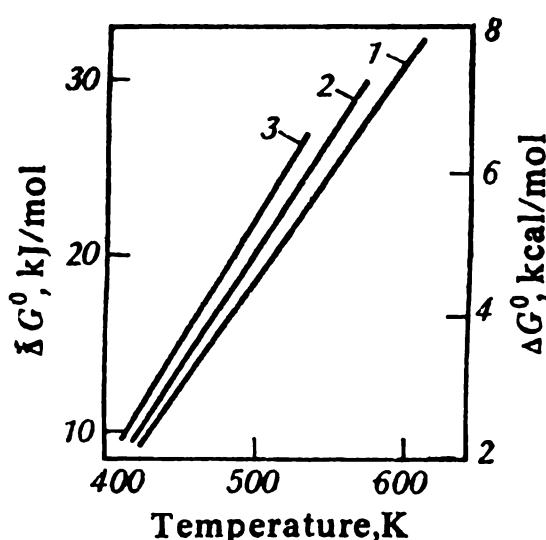


Fig. 3.5. Temperature dependence of the free-energy change for hydration of ethylene (1), propylene (2), and isobutylene (3).

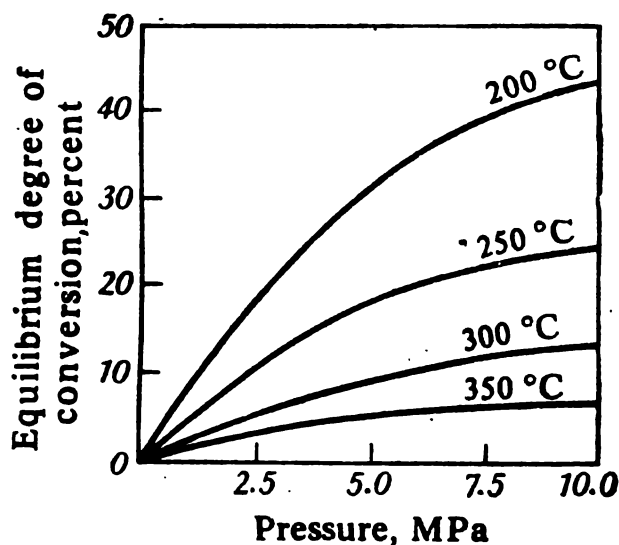
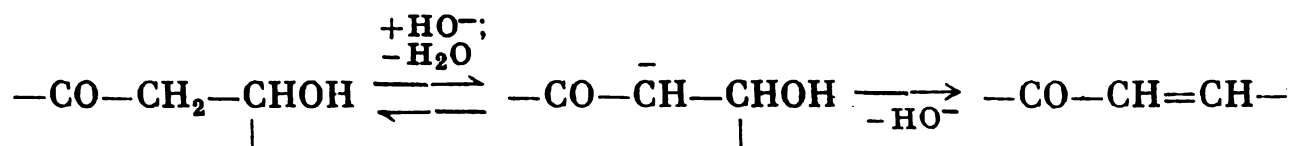


Fig. 3.6. Dependence of the equilibrium degree of conversion of ethylene to ethyl alcohol on pressure at various temperatures and a $\text{C}_2\text{H}_4/\text{H}_2\text{O}$ ratio of 1 : 1.

be controlled thermodynamically by changing the pressure: the formation of an ether is not affected in this way, but a decrease in pressure favours the formation of an olefin.

Catalysis, Mechanism and Kinetics of the Reactions. All the reactions under consideration belong to the category of acidic-catalytic processes. The typical hydration catalysts are sufficiently strong protic acids: phosphoric acid on a support, polytungstic acid, sulphonic cation-exchangers. For dehydration, use is made of supported phosphoric acid, aluminium oxide, sulphuric acid, phos-

of the reaction by bases:



For heterocatalytic intra- and intermolecular dehydration in the gas phase the kinetics of the process is described by the following equations, respectively:

$$r_{\text{olef}} = \frac{kP_{\text{alc}}}{P_{\text{alc}} + KP_{\text{H}_2\text{O}}} \quad \text{and} \quad r_{\text{eth}} = \frac{k \left(P_{\text{alc}}^2 - \frac{1}{K_p} P_{\text{eth}} P_{\text{H}_2\text{O}} \right)}{P_{\text{alc}} + KP_{\text{H}_2\text{O}}}$$

These equations take into account the irreversibility of intramolecular dehydration and the retarding effect of alcohol and water, which are better adsorbed at the active sites of the catalyst.

In the hydration of olefins the water is always present in some excess, which is why the retarding effect of the alcohol may be neglected:

$$r_{\text{ROH}} = \frac{k \left(P_{\text{olef}} P_{\text{H}_2\text{O}} - \frac{1}{K_p} P_{\text{alc}} \right)}{P_{\text{H}_2\text{O}}} = k \left(P_{\text{olef}} - \frac{1}{K_p} \cdot \frac{P_{\text{alc}}}{P_{\text{H}_2\text{O}}} \right)$$

In a number of cases the role of water is more complicated. For example, phosphoric acid applied onto a porous support forms on its surface a liquid film, which absorbs water from the gas phase. In the gas phase a phase equilibrium sets in at each specified temperature and partial pressure of the water vapours, and phosphoric acid in the film has a certain definite concentration and a corresponding catalytic activity. The latter falls off with decreasing temperature and increasing partial pressure of water, which limits the choice of these parameters to various extents in each particular case.

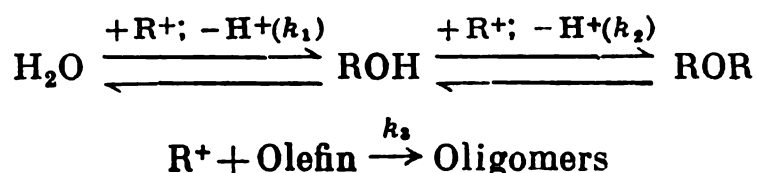
For the catalysis of hydration-dehydration reactions using sulphonic cation-exchangers the following kinetic equation has been found:

$$r = \frac{kC_{\text{sc}}}{1 + K_{\text{sc}}C_{\text{sc}} + (K_{\text{H}_2\text{O}}C_{\text{H}_2\text{O}})^2} + k'C_{\text{sc}}$$

The first term corresponds to catalysis effected by means of the sulpho groups of the cation-exchanger and the second to specific catalysis carried out using the hydroxonium ions, H_3O^+ . If the amount of water in the mixture is small, the first term, which is strongly dependent on the water concentration, is dominant; an increase in this quantity leads to the predominance of the second term.

Side Reactions and Process Selectivity. In the hydration of olefins, the main reaction is accompanied by the oligomerization of an olefin (low-molecular-weight polymers are formed) and the formation of an ether. All these reactions proceed via the intermediate carbon-

ium-ion step, which may be sketched by the following scheme:

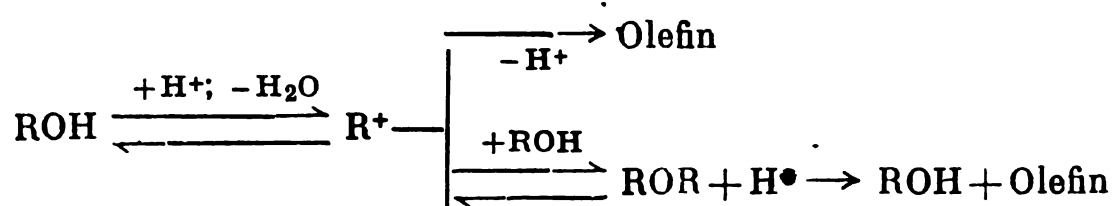


For a state of the system far from equilibrium this scheme yields the following equation for differential selectivity:

$$\varphi_{\text{ROH}} = \frac{d[\text{ROH}]}{d[\text{Olefin}]} = \frac{1 - \frac{k_2}{k_1} \cdot \frac{[\text{ROH}]}{[\text{H}_2\text{O}]}}{1 + \frac{k_3}{k_1} \cdot \frac{[\text{Olefin}]}{[\text{H}_2\text{O}]}}$$

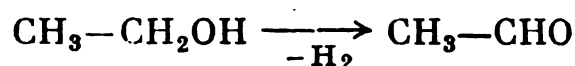
From this equation it is seen that the selectivity increases in the presence of excess water with respect to the olefin and the alcohol formed. The alcohol is more reactive than water $[(k_2/k_1) > 1]$, which is why the reaction must be carried out so as to maintain a large excess of water with respect to the alcohol (at about 15 : 1). The yield of oligomers depends on the tendency of olefins to undergo polymerization (isobutylene > propylene > ethylene). The formation of oligomers can be reduced not only by changing the water-olefin ratio but also by lowering the temperature, since oligomerization has a higher energy of activation than hydration. It should be noted that upon approach to equilibrium the rate of hydration and the selectivity fall off, which makes it unprofitable to bring the reaction to near-equilibrium degrees of conversion. Here, for each olefin and catalyst there is a certain optimum of the ratio of the reactants, degree of conversion and temperature, which depends on the productivity and selectivity of the process.

A scheme of conversions has been found for the dehydration of alcohols, according to which an ether is capable of decomposition into an olefin and alcohol:



Intramolecular dehydration has a higher activation energy than the formation of an ether. From this and also from the consideration of the above-given scheme it follows that dehydration involving the formation of an unsaturated bond must be carried out at elevated temperature and low partial pressure or concentration of alcohol. The dehydration involving the formation of an ether is carried out at a lower temperature, higher concentrations and partial pressures of alcohol (say, under some pressure) and with an incomplete conversion of the alcohol in the reactor.

As a result of the reactions considered, not infrequently another product is also formed, namely an aldehyde or ketone, the formation of which is a consequence of the dehydrogenation of alcohol:



Protic acid do not catalyze this reaction, but it becomes feasible through the use of certain supports or oxide catalysts. The most selective oxide catalysts for dehydration (as compared with dehydrogenation) are ThO_2 and Al_2O_3 , whereas many of the oxides have a mixed action and others are predominantly dehydrogenation catalysts.

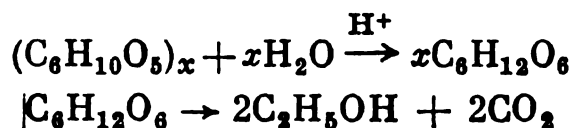
3.2.2. Hydration of Olefins and Acetylene

The hydration of olefins is employed for the manufacture of many products.

Ethyl alcohol (ethanol), $\text{C}_2\text{H}_5\text{OH}$, is a liquid which boils at 78.3°C ; it forms explosive mixtures with air within the concentration limits of 3-20 percent by volume. With water ethyl alcohol gives an azeotropic mixture which contains 95.6 percent of alcohol and boils at 78.1°C . It is in this form that ethanol is commonly used for practical purposes.

Ethyl alcohol belongs to the category of the largest multitonnage and extensively used products of organic synthesis. It is a good, though flammable, solvent; large amounts of ethyl alcohol are used in food and drug industry; it serves as a fuel in liquid-fuel jet engines, as an antifreeze, etc. As an intermediate of organic synthesis ethanol is of value for the production of esters, chloroform, chloral, diethyl ether, acetaldehyde and acetic acid.

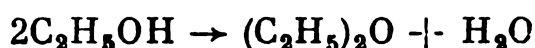
Until recently the production of ethyl alcohol has been based on the fermentation of starch from certain grains and potato using enzymes obtained from yeast fungi. This method is still used at present but it requires large amounts of food raw materials and cannot meet increasing demands for the alcohol. Another method, which is also based on the processing of plant raw materials consists of the hydrolysis of wood. Wood contains up to 50 percent cellulose, whose hydrolysis with water in the presence of sulphuric acid yields glucose, which is then subjected to alcoholic fermentation:



Synthetic ethyl alcohol is produced by the hydration of ethylene.

Diethyl ether (sulphuric ether), $(\text{C}_2\text{H}_5)_2\text{O}$, is a liquid boiling at 34.6°C . It is used chiefly as a solvent, but its high flammability is a disadvantage. Limited amounts of diethyl ether is employed

in medicine. Diethyl ether is formed as a by-product in the hydration of ethylene, but the amount produced does not satisfy the demand for it, which is why it is specially synthesized from ethyl alcohol



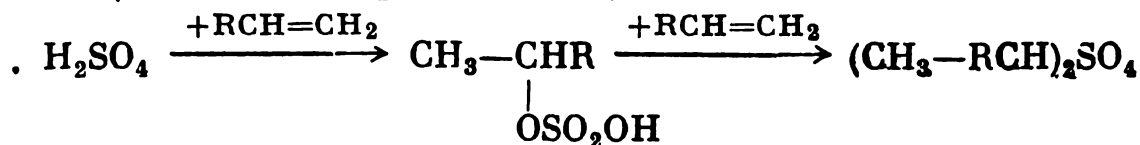
Isopropyl alcohol, $\text{CH}_3\text{—CHOH—CH}_3$, is a liquid (b.p. 82.5°C) which is miscible with water. Its vapours form explosive mixture with air within the concentration limits of 2-12 percent (by volume). Isopropyl alcohol gives with water an azeotropic mixture containing 88 percent of the alcohol and boiling at 80.3°C . Isopropyl alcohol has found application as a solvent, which often replaces ethyl alcohol. Besides, it is used to produce esters, acetone, etc. Isopropyl alcohol is exclusively manufactured synthetically, namely, by the hydration of propylene.

Secondary butyl alcohol, $\text{CH}_3\text{—CHOH—CH}_2\text{—CH}_3$ (b.p. 99.5°C) and *tertiary butyl alcohol* $(\text{CH}_3)_3\text{COH}$ (b.p. 82.8°C) are colourless liquids (the former is sparingly soluble in water and the latter is miscible with water in all proportions). Both compounds form with water azeotropic mixtures, which contain 68 and 78 percent of alcohol, respectively. *sec*-Butyl alcohol is of greater value than *tert*-butyl alcohol. It is used as a solvent and also for the production of esters and methyl ethyl ketone, $\text{CH}_3\text{—CO—CH}_2\text{—CH}_3$. These alcohols are prepared, respectively, by the hydration of 1-butene and 2-butene or isobutylene, including the C_4 fraction freed from butadiene.

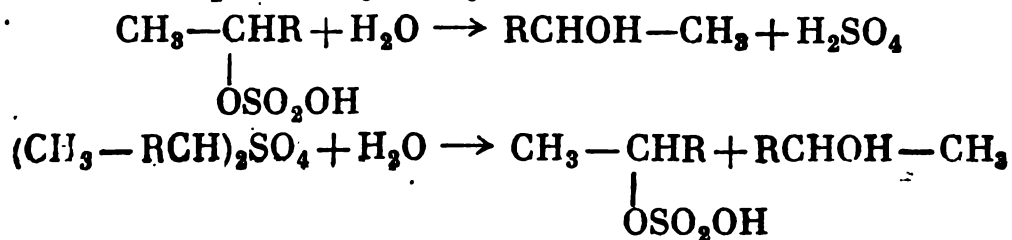
The ethers of isopropyl and *sec*- and *tert*-butyl alcohols obtained as by-products in the hydration of the corresponding olefins find application as solvents. Of these ethers, *diisopropyl ether*, $[(\text{CH}_3)_2\text{CH}]_2\text{O}$ is the most important; it is less flammable than diethyl ether and can often replace it as a solvent.

3.2.2.1. Sulphuric-Acid Hydration of Olefins

This was the first method of hydration of olefins; it is still used at present. In this process, olefins are preliminarily absorbed in sulphuric acid, which leads to the formation of alkyl and dialkyl sulphates (esters of sulphuric acid):



and to their subsequent hydrolysis with water:



Depending on the reactivity of olefins and in order to suppress the side polymerization, absorption is effected under different conditions: the concentration of sulphuric acid ranges from 60 up to 98 percent, the temperature is varied from 0 up to 70 °C, and the pressure range is from 0.2 up to 2 MPa (the first figures refer to isobutylene and the second to ethylene). The ratio of sulphuric acid to an olefin is such that 1.2-1.3 moles of olefin is absorbed per 1 mole of H_2SO_4 , which cuts down the consumption of the acid. Under such conditions and also because of the hydrolysis of the sulphates with

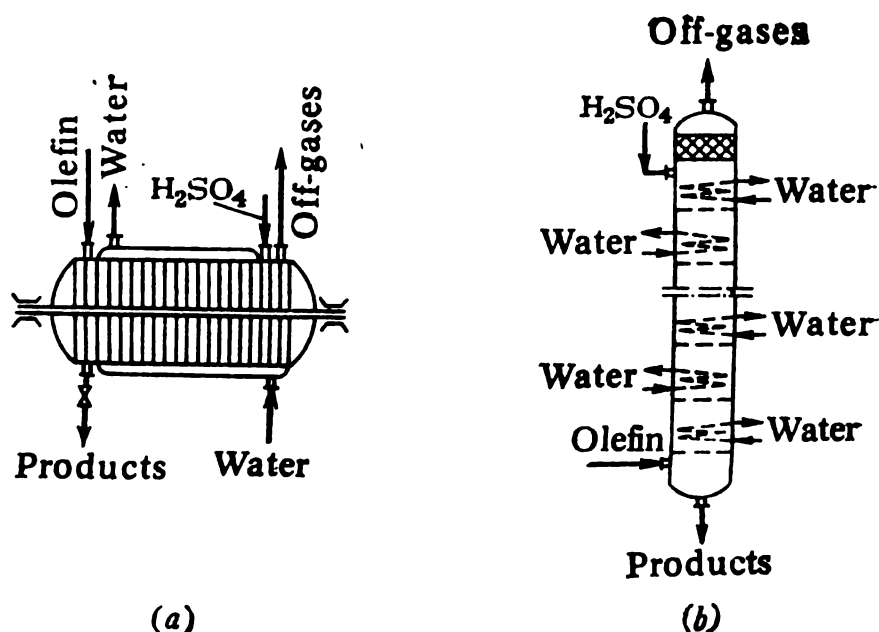


Fig. 3.7. Reactors for sulphuric-acid hydration of ethylene and propylene: a—horizontal absorber with a disk mixer; b—continuous column-type tray absorber.

the water contained in the sulphuric acid, the reaction mass consists of alkyl and dialkyl sulphates, H_2SO_4 , water, alcohol and an ether and polymers, the last two being by-products.

Two types of reaction vessels are used for the absorption of ethylene and propylene. One is a horizontal absorber with a stirrer, which is equipped with a large number of disks (Fig. 3.7a). The inner space of the absorber is about one-third filled with sulphuric acid, which forms a fog upon rotation of the disks, which increases the phase contact surface. The reaction heat is removed by the water circulating in the jacket. This absorber operates batchwise, but the use of a cascade of several absorbers makes it possible to carry out a continuous process.

Continuous column-type absorbers equipped with 20-25 cap trays (with the liquid being at a high level) are more efficient (see Fig. 3.7b). There is a tubular cooler at each tray in the liquid layer; cold water is circulated through the cooler, which provides the removal of the heat evolved. Fresh sulphuric acid of required concentration is fed to the upper tray of the column, and the reaction mass of specified composition is taken from the still. Ethylene (or propylene) moves

upwards countercurrently to the liquid, bubbles through a layer of sulphuric acid at each tray and leaves the top of the column being considerably diluted with the inert impurities from the starting gas.

There is a packing at the upper part of the column which plays the role of a spray trap.

The reaction mass obtained at the first stage passes then to the sulphate hydrolysis stage. The liquid is diluted with water and heated by live steam, in the current of which alcohol, ether and polymers are distilled off. These are separated by settling and fractionation, as a result of which the alcohol is produced with a yield of 90 percent. The sulphuric acid left after the hydrolysis has a concentration of 40-50 percent. It is used for the production of ammonium sulphate or is concentrated to be returned to the absorber and to be recycled. The presence of this spent acid, which must be regenerated and re-used is the main disadvantage of the sulphuric-acid hydration of olefins.

•A variant of this process is the sulphuric-acid method of extraction of isobutylene from the C_4 fractions (page 57); a distinctive feature of this process is that the alcohol and the alkyl sulphate contained in the mixture are subjected to an elimination reaction to give not the alcohol but isobutylene, which is the major product.

3.2.2.2. Direct Hydration of Olefins

The above disadvantages of the sulphuric-acid method have led to the development of methods of direct hydration of olefins, which consists of the direct addition of water across the double bond in the presence of acid catalysts. The advantages of these methods are as follows: the process takes place in one step, sulphuric acid is not used and there is no need to use units for its regeneration, the alcohol yield is high (about 95 percent), and the less corrosion of the apparatus.

The catalyst most frequently used for this process is phosphoric acid on a solid support (highly porous silica gel, aluminosilicate). The choice of the process parameters and the factors mentioned above are dictated by economic considerations, especially by the reduction of energy consumption for the generation of steam and for the recirculation of the unconverted compounds. The temperature has an opposite effect on the equilibrium and rate of the process; besides, an increase in temperature results in an increased polymerization of the olefin and in a loss of phosphoric acid from the support. Therefore, the hydration of ethylene is carried out at 260-300 °C, when a high partial pressure of steam (2.5-3 MPa) is required to maintain the desired concentration of H_3PO_4 in the surface film of the catalyst. In order to increase the degree of conversion of steam, to obtain the

alcohol not too much diluted and to lower the consumption of energy, operation is carried out in some excess of ethylene [(1.4-1.6) : 1]. This dictates the choice of the total pressure (7-8 MPa) at which the equilibrium degree of conversion is 8-10 percent. The actual degree of conversion is, however, maintained at the level of 4 percent, which enables the process to be conducted at sufficiently high space velocities (2000 h⁻¹) and unit capacity of the catalyst with respect to the alcohol [180-220 kg/(m³·h)], the 15-percent ethanol being obtained after the condensation.

The dilution of the olefin with inert impurities has an unfavourable effect on the equilibrium and rate of the process. Therefore, in contrast to the sulphuric-acid hydration, the starting olefin must be sufficiently concentrated (97-99 percent). When it is recirculated, inert impurities are gradually accumulated in it; the permissible maximum concentration of the olefin in the recycle gas is 85 percent. In order to maintain this concentration, a purge has to be taken from the recycle gas.

The reaction is carried out in a continuous unit called the hydrator. This is a hollow steel column 1.5 m in diameter and 10 m high. In order to prevent the corrosion by the action of phosphoric acid, the hydrator is lined with red-copper sheets. The catalyst is poured into the reactor in several layers over the supporting perforated cone. The mixture of the olefin and water vapours preheated to the reaction temperature flows downwards, passes through the catalyst bed and is removed from the lower part of the hydrator. Because of the low degree of conversion and the low reaction heat, no special cooling of it is required in the apparatus.

In the course of the hydration process phosphoric acid is gradually removed from the support surface and in 400-500 hours of operation the catalyst loses its activity. In order to lengthen the life of the catalyst, it must be impregnated with fresh phosphoric acid. However, in this case too, the catalyst has to be replaced in a certain period of time because tarry deposits are formed on its surface and the catalyst support becomes extremely brittle. A fresh catalyst is prepared by impregnating the support with 60-65-percent phosphoric acid with subsequent drying at 100° C. It contains 35 percent of free phosphoric acid.

The Flow Diagram of Ethanol Synthesis. Because of the low degree of conversion and high temperature and pressure in the direct hydration of ethylene, the recirculation of the stream and energy consumption are of prime importance. The existing schemes of the process differ considerably, especially by the source of steam needed for synthesis and by the degree of purification of the end product. Steam of the appropriate parameters is not infrequently supplied from external sources (as is the practice in the USSR) or produced *situ* in a tubular furnace. In the latter case, the closed water

circuit system is realized. The flow diagram of such a process is given in Fig. 3.8.

Fresh and recycle ethylene is compressed up to 8 MPa in compressor 1 and circulation compressor 2, mixed with the recycle water condensate and heated in heat exchanger 4 by the hot reaction gases. The mixture is then additionally heated up to 280-330°C in tubular furnace 3 and introduced into reactor 5. The reaction gases contain vapours of phosphoric acid, which are preliminarily neutralized by injecting an aqueous solution of NaOH. The phosphoric acid

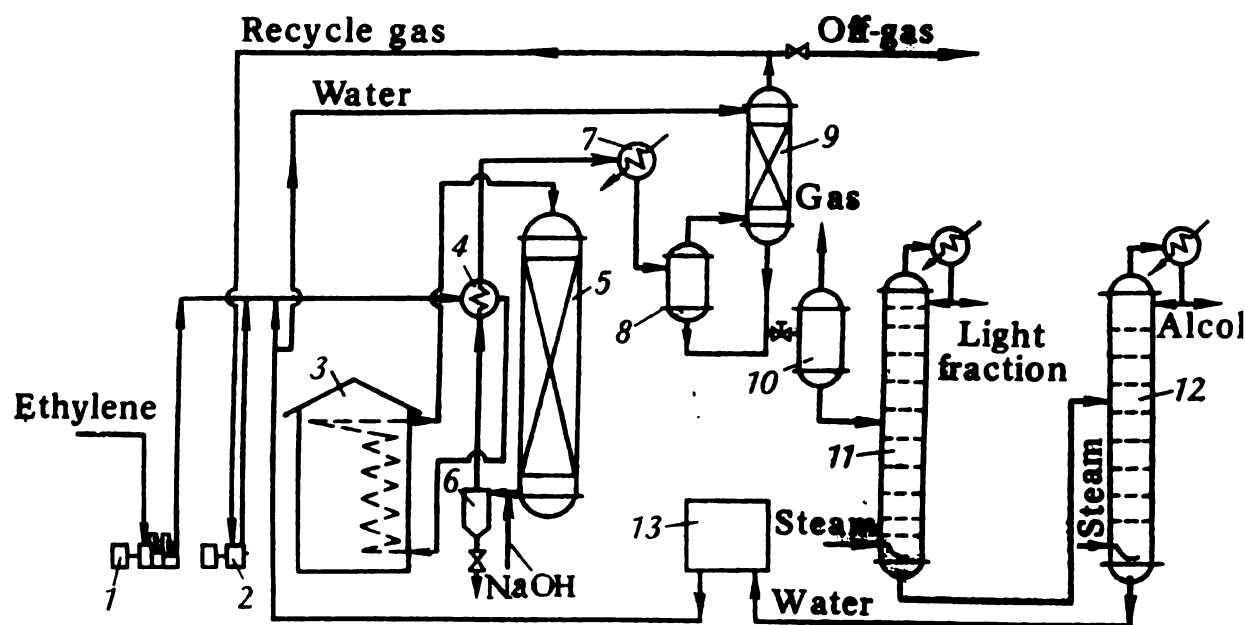


Fig. 3.8. Flow diagram of ethanol production:

1, 2—compressors; 3—tubular furnace; 4—heat exchanger; 5—reactor; 6—salt separator; 7—cooler; 8, 10—separators; 9—absorber; 11—column for separation of the light fraction; 12—ethanol column; 13—unit for ion-exchange purification of recycle water.

formed are separated in salt-separation unit 6. The heat of the gases is utilized in heat exchanger 4 and after additional cooling in water cooler 7 the liquid and gas phases are separated in high-pressure separator 8.

The gases still contain alcohol vapours, which are trapped by water in absorber 9. The gas freed from the alcohol is recycled by means of compressor 2, but part of it is discharged into the fuel gas stream in order to avoid excessive accumulation of the inert impurities. The water condensate leaving separator 8 and the liquid from absorber 9 are throttled and separated in a low-pressure separator from dissolved gases, which are used as fuel. The 15-percent ethanol solution containing diethyl ether, acetaldehyde and low-molecular weight polymers of ethylene leaves separator 10. This solution is subjected to fractionation in columns 11 and 12. The most volatile diethyl ether and acetaldehyde are distilled out in the first column and ethyl alcohol in the second (ethyl alcohol is distilled off as an azeotropic mixture containing 95 percent of alcohol and 5 percent of water), the heating being effected with live steam. In the

column 12 water is left, which is purified in ion-exchange unit from the salts and returned for mixing with ethylene and to the hydration unit; a closed water circuit system is thus realized.

Synthesis of Isopropyl Alcohol. The methods of direct hydration of propylene are more diverse than those used for ethylene. There is gas-phase hydration in the presence of a phosphoric-acid catalyst which is analogous to the process used for the synthesis of ethyl alcohol. Because of the high reactivity of propylene, the reaction temperature is about 200 °C at which the equilibrium is more favourable for hydration. Therefore, the pressure can be reduced down to 1 MPa. In order to avoid excessive formation of diisopropyl ether, the degree of conversion of water vapours has to be limited to the order of 4-5 percent, which allows the 15-20-percent alcohol to be condensed out. Conversely, the degree of conversion of propylene may be substantially higher, being achieved by controlling the composition of the feed mixture: when isopropyl alcohol is to be produced, in contrast to the hydration of ethylene, excess water is used and the degree of conversion of propylene is kept up to 10-12 percent. This considerably improves the technical and economic indices of the reaction as compared with the direct hydration of ethylene and especially with the sulphuric-acid method.

The catalyst used in the liquid-phase hydration of propylene is a sulphononic cation-exchanger (a sulphonated copolymer of styrene and divinyl benzene; the particle size is 0.2-0.9 mm). It is active for the hydration of propylene even at temperatures of 130-150 °C. At a pressure of 6-10 MPa and a molar ratio of $\text{H}_2\text{O}/\text{C}_3\text{H}_6 = 12.5-15$:1 the degree of conversion of propylene amounts to 10 percent. In one of the large plants in FRG the yield of alcohol and ether is, respectively, 94 and 3.5 percent with the catalyst's service life being 8 months. The synthesis is carried out in a column reactor with four catalyst beds (Fig. 3.9) with a direct-flow (downward) movement of the propylene gas and water, which flows over the catalyst grains. The temperature is controlled through the removal of the heat evolved by passing a slightly heated part of the water between the catalyst beds. At the same time, this enables the development of a temperature profile close to the optimum for the

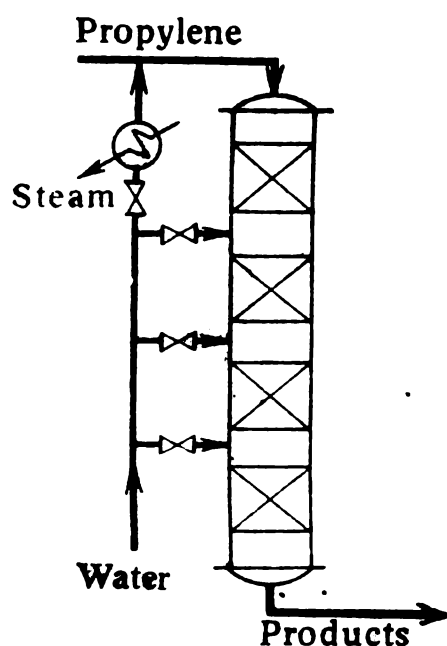


Fig. 3.9. Reaction unit for hydration of propylene on a sulphononic cation-exchanger.

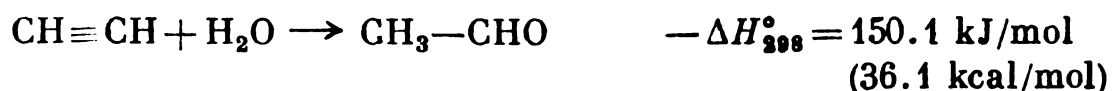
reversible exothermic reaction; this temperature profile decreases as the reaction is continued.

A further gas-phase process is based on the use of a polytungstic acid catalyst at 240-270 °C and 15-20 MPa with the degree of conversion of propylene being 60-70 percent and the selectivity with respect to isopropyl alcohol reaching 98 percent.

Just as isopropyl alcohol, *sec*-butyl alcohol can also be produced by the direct hydration of *n*-butylenes. There is also a method of direct hydration of isobutylene over a sulphonic cation-exchange resin which is a step in the processing of the C₄ fractions and which is used to derive isobutylene.

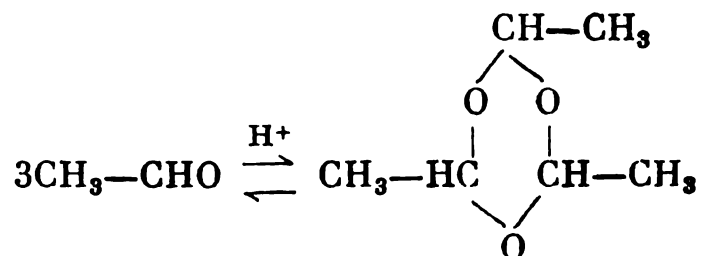
3.2.2.3. Hydration of Acetylene

The hydration of acetylene according to the Kucherov method



has been for a long time the only industrial method of manufacture of acetaldehyde, but today there is a more efficient method of synthesis from less expensive ethylene. Because of this, the hydration of acetylene has lost its importance, though the older plants designed for producing acetaldehyde from acetylene are still operating.

Acetaldehyde is a volatile liquid (b.p. 20.8 °C), which is completely miscible with water and forms with air explosive mixtures with the concentration limits of 4-57 percent (by volume). It is used on a large scale for the production of acetic acid, acetic anhydride, *n*-butyl alcohol, pentaerythritol, C(CH₂OH)₄ and other valuable products. In the presence of acids it gives a liquid cyclic trimer called *paraldehyde*:

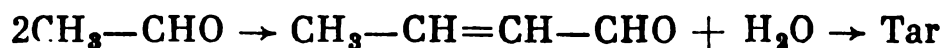


The reaction is reversible, which is why paraldehyde can be used in many cases instead of acetaldehyde.

Hydration Using a Mercury Catalyst. This method proposed by M. G. Kucherov is carried out in the liquid phase by bubbling acetylene through 10-20-percent sulphuric acid containing 0.5-0.6 percent of HgO, which is present in solution in the form of HgSO₄.

Under these conditions, the hydration of acetylene is accompanied by two side reactions: the condensation of acetaldehyde with th

formation of crotonaldehyde and tar:



and the reduction of mercury salts by acetaldehyde, these salts being converted to an inactive form:



The extent of these side reactions can be reduced considerably by lowering the concentration of the aldehyde in the reaction liquid. This is achieved by continuous purging of the acetaldehyde formed in the current of the unconverted acetylene, which is introduced into the reaction in a 2-2.5-fold excess.

Since the reduction of mercury salts and their rapid deactivation are highly undesirable, use is made in practice of another method for increasing the service life of the catalyst. A ferric salt capable of oxidizing the reduced form of mercury again to the divalent state is added to the reaction solution:



The ferric salt is added in excess with respect to mercury (about 4 percent on Fe_2O_3), which is why the catalyst solution is active for sufficiently long time. However, ferrous salts are gradually accumulated in it, and the solution is sent to regeneration, which consists of the oxidation by nitric acid. In spite of all these measures, mercury is still lost as a sludge together with the resinification products. Its consumption is 1-1.5 kg per 1 ton of acetaldehyde.

The reaction unit used for the gas-phase hydration of acetylene is shown schematically in Fig. 3.10a. The reactor is a hollow column lined with acid-resistant materials and having in the upper flared part a packing layer, which serves as a spray trap. The reactor is filled with a catalyst liquid of the composition described above, through which the acetylene introduced into the bottom of the column is bubbled. The reactor has no heat-exchange surfaces and operates at 90 °C under autothermal conditions: the heat evolved is removed by evaporation of water, which is condensed in a reflux condenser and is returned to the reactor. Part of the catalyst solution is continually withdrawn for regeneration and replaced by the regenerated solution. Acetaldehyde is absorbed by water from the gas-vapour mixture leaving the reaction unit, the acetylene is returned to the reaction and the aqueous solution of acetaldehyde is subjected to fractionation.

Hydration Using Nonmercury Catalysts. One of the main disadvantages of the method described above is the use of toxic and expensive mercury salts as catalysts. It is for this reason that nonmercury catalysts have for a long time been sought for. Such catalysts are phosphoric acid, and magnesium, zinc and cadmium phosphates.

All these catalysts are less active than mercury salts and are used only at high temperatures as heterogeneous catalysts. Of these compounds, wide use is made of a mixture having the composition $\text{CdHPO}_4 \cdot \text{Ca}_3(\text{PO}_4)_2$, which has acidic properties and which contains a metal of the same group of the Periodic System as mercury. This mixture is active at 350–400 °C.

In the gas-phase hydration of acetylene it is impossible to remove acetaldehyde as it is formed, which is why the reaction of croton

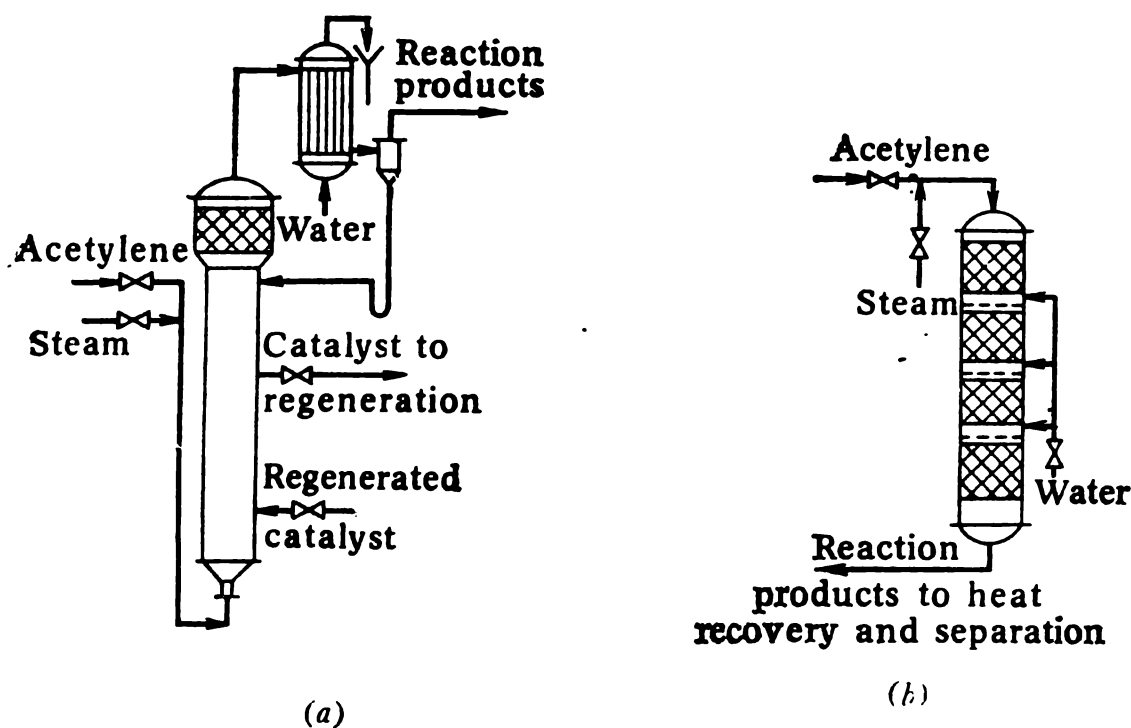


Fig. 3.10. Reaction units for acetylene hydration:

a—liquid-phase process with a mercury catalyst; *b*—gas-phase process with a heterogeneous nonmercury catalyst.

condensation becomes especially hazardous. It has a higher activation energy than hydration and therefore one of the ways of increasing the selectivity is to eliminate overheating and to develop optimal thermal conditions. Another way is to use a large excess of steam and to avoid the incomplete conversion of acetylene in the reactor, which speeds up the hydration and at the same time slows down the croton condensation of the aldehyde. With a volume ratio of steam to acetylene of (7–10) : 1 and a degree of conversion of acetylene ranging from 40 to 50 percent the yield of acetaldehyde is 89 percent, the by-products formed being 6–7 percent of crotonaldehyde, 0.5–1 percent of acetic acid and 0.3 percent of acetone.

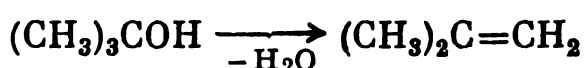
The gas-phase hydration of acetylene is carried out in a column-type reactor containing several continuous catalyst beds (see Fig. 3.10*b*). The preheated mixture of steam and acetylene is introduced into the upper part of the reactor and the reaction gases are taken from the bottom for condensation and separation. The reactor has no heat-exchange surfaces—the heat evolved is removed through

evaporation of the water condensate, which is sprayed into the space between the catalyst beds. They are separated, in addition, by cap trays which prevent the sprays to fall onto the succeeding catalyst beds.

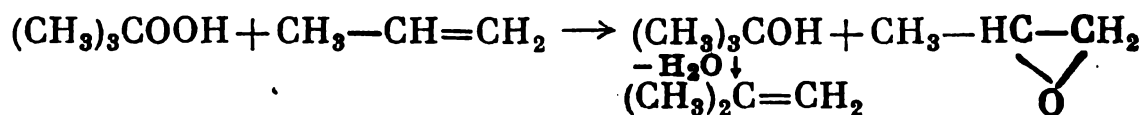
Apart from the relatively low yield of acetaldehyde, the major disadvantage of the gas-phase hydration of acetylene is the short service life of the catalyst—it has to be regenerated every 100 hours. With this being taken into account, the overall service life of the catalyst is only 2500 hours.

3.3. Dehydration Processes

Dehydration Involving the Formation of Unsaturated Compounds. This process was formerly used for the manufacture of lower olefins from the corresponding alcohols, for which purpose either liquid-phase sulphuric-acid catalysis was carried out at 100-160 °C or a gas-phase process over an aluminium oxide (Al_2O_3) catalyst at 300-400 °C. Since there are cheaper sources of lower olefins, the process is of value today only for the production of isobutylene. One of its variants is used for the extraction of isobutylene from the C_4 fractions of cracked gases and pyrolysis gases (see page 58); one of the steps is the dehydration of *tert*-butanol upon catalysis with sulphuric acid or a sulphonic cation-exchanger:

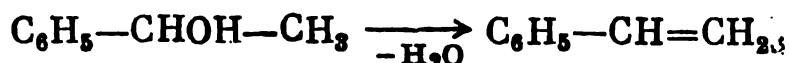


In another variant, the dehydration involving the formation of isobutylene is carried out with *tert*-butanol formed in the hydroperoxide method of manufacture of propylene oxide:



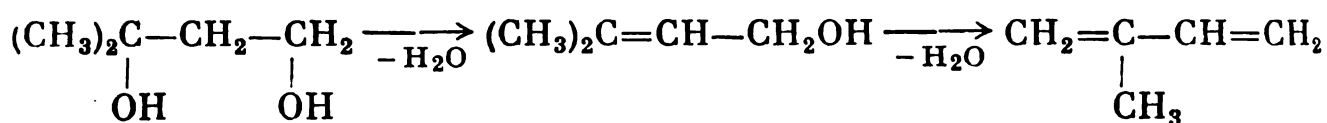
In this and other cases, the dehydration involving the formation of unsaturated compounds is most often one of the steps in the production of many monomers.

For example, in one of the new processes styrene is made by the dehydration of methylphenylcarbinol:

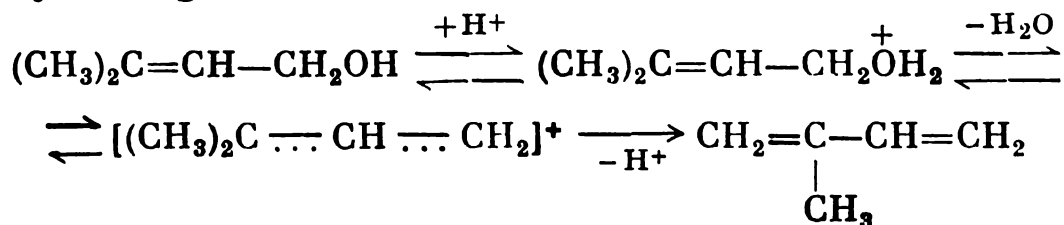


The well-known method of synthesis of isoprene from isobutylene and formaldehyde is also based on the final dehydration of a diol

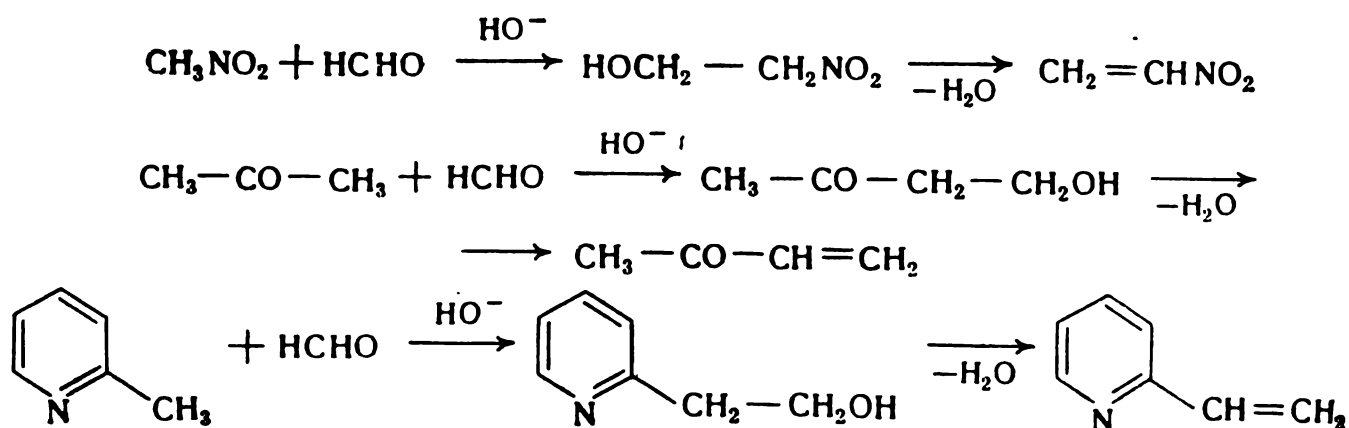
and an unsaturated alcohol:



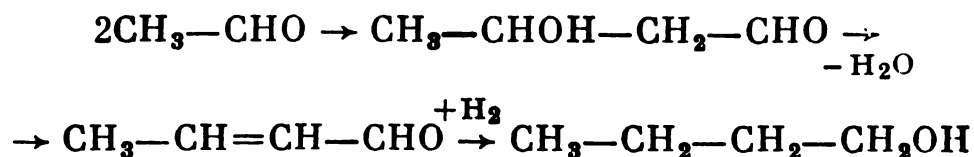
When the first water molecule is eliminated from the diol, a mixture of unsaturated alcohols of different composition is formed, but upon further dehydration they all give isoprene, the reaction being accompanied by a migration of the double bonds:



Another route for the production of unsaturated compounds is to introduce a vinyl group by way of aldol-type condensation reactions followed by dehydration. It may be illustrated by the example of the synthesis of nitroethylene, vinyl methyl ketone and 2-vinyl pyridine:



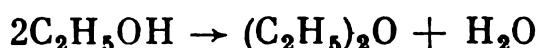
Dehydration is also one of the steps in the production of esters of methacrylic acid, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COOR}$, some primary alcohols, say *n*-butanol:



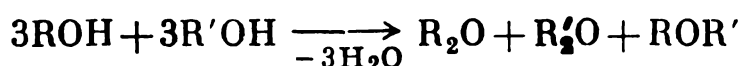
2-ethylhexanol, methyl isobutyl ketone, and many other compounds to be described further in the text.

Dehydration Involving the Formation of Ethers. We have already mentioned the formation of by-product ethers in the hydrolysis of chloro derivatives (Sec. 3.1.1) and in the hydration of olefins (see Sec. 3.2.1). These processes provide all the required amount of ethers, such as diisopropyl ether. However, diethyl ether has found wide application and it is specially produced by the intermolecular de-

dration of ethanol at 250 °C over a heterogeneous catalyst (Al_2O_3):



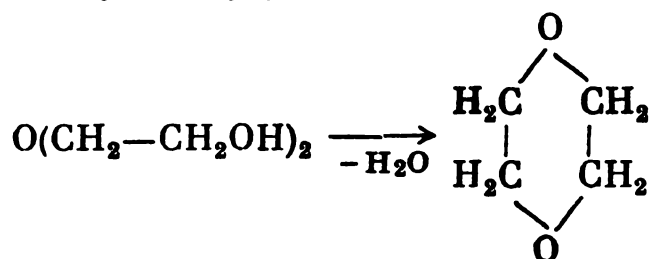
The possibility of using this method for the synthesis of ethers from isopropyl and higher alcohols is limited by the formation of by-product olefins. As a result, most olefins are obtained in the liquid phase at a lower temperature using acid catalysts—sulphuric, phosphoric and arylsulphonic acids. The method is suitable chiefly for the synthesis of symmetrical ethers having identical alkyl groups since upon dehydration of a mixture of two alcohols the yield of a mixed ether is not high:



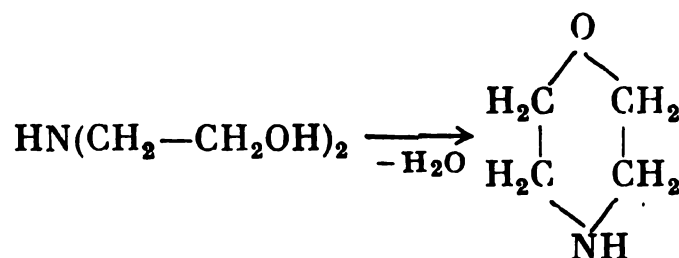
Of the symmetrical ethers with a straight chain of carbon atoms, β' -dichlorodiethyl ether (*Chlorex*) is a valuable solvent and extractant and also the starting material for the production of polysulphide polymers. Dichlorodiethyl ether is made by the dehydration of hydrous ethylenechlorohydrin over an acidic acid catalyst:



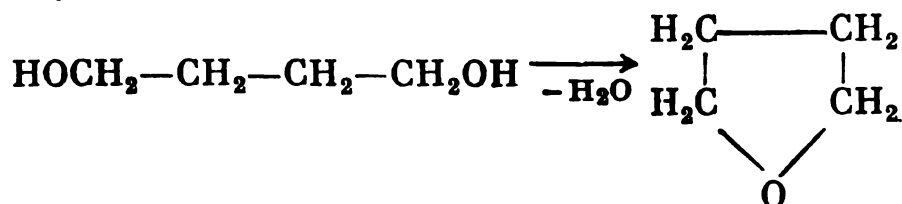
Dihydric alcohols when subjected to acid catalysis are capable of cyclization to stable five- or six-membered rings. In this way, *dioxane* is made from diethylene glycol



Morpholine from diethanolamine:



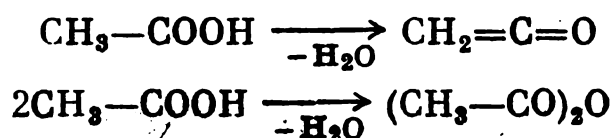
and *tetrahydrofuran* from 1,4-butanediol:



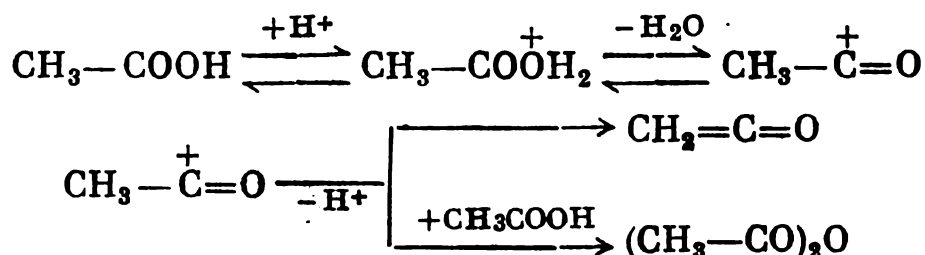
These compounds are all used as solvents.

Dehydration of Carboxylic Acids. This process holds a somewhat special position among the other dehydration processes. The products of intra- and intermolecular dehydration are ketene and acetic

anhydride:



These reactions are endothermic and their equilibrium is shifted to the right only at a high temperature: 500-600 °C for the preparation of the anhydride and 700 °C for ketene. Note that in the formation of ketene the equilibrium conversion is also favoured by a low pressure. Both reactions proceed in the presence of heterogeneous acid-type catalysts (metal phosphates and borates) or of vapours of phosphoric acid, which may be introduced into the feed mixture in the form of esters readily hydrolyzable to the free acid. The mechanism of the reactions is in general similar to other dehydration processes:



Ketene is a gas with a pungent odour, which is capable of being condensed to a liquid at -41°C . It is highly reactive, interacts with various compounds with the formation of acetic acid and its derivatives. In particular, with acetic acid it gives acetic anhydride:



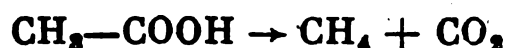
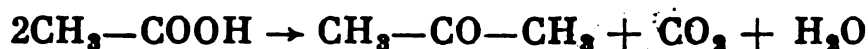
Acetic anhydride is a liquid having a pungent odour (b.p. 141°C). It is an important product of organic synthesis and is widely used as an acetylating agent in the syntheses of acetic acid esters which are difficult to obtain by other routes—phenol acetates, acetates of tertiary alcohols and especially cellulose acetate and acetate fibre.

Acetic anhydride was formerly produced by the chlorine method, from sulphuryl chloride and sodium acetate:



Because of the consumption of large amounts of reagents and formation of salt wastes this method has been superseded by the dehydration of acetic acid. The process can be accomplished by two routes: intermolecular dehydration or via the intermediate formation of ketene. In both cases, the gas mixture obtained contains very reactive acetic anhydride or ketene and water, which can easily be converted on cooling back to acetic acid. Therefore, the water must be separated from the reaction gases so as to prevent it from reacting with ketene or acetic anhydride. In the direct synthesis of acetic anhydride, this is achieved by rapid cooling of the reaction

gas with addition of an azeotropic component (ethyl acetate), which is separated together with water from the condensate, which is then separated into acetic anhydride and acetic acid. In the method involving the intermediate formation of ketene the reaction gases are rapidly cooled down to 0 °C and the unconverted acetic acid and water are condensed out from them. The gas left is passed through the column refluxed with acetic acid, where acetic anhydride is formed. The by-products formed in these reactions are acetone and methane:



but the yield of acetic anhydride is sufficiently high and amounts to 90 percent.

3.2.3.1. Technology of Dehydration Processes

Dehydration processes are carried out by two principal methods: in the liquid and in the gas phase.

Liquid-phase dehydration is used in those cases where the product or reactants are insufficiently stable at elevated temperatures of the gas-phase process. This refers to the synthesis of Chlorex, dioxane and morpholine, but in the liquid phase nitroalcohols, hydroxy-aldehydes and hydroxy ketones also often undergo dehydration; these compounds can be converted to the corresponding unsaturated compounds in the gas phase too. The catalysts used are sulphuric acid (in concentrations of up to 70 percent), phosphoric acid, acid phosphates of calcium or manganese, sulphonic cation-exchangers (the last-named compounds are used at a temperature of up to 150 °C). The process is carried out at temperatures from 100 to 160-200 °C under ordinary pressure.

Liquid-phase dehydration (Fig. 3.11a) is most often operated as a continuous process by two principal methods. In one, the process is carried out by continually distilling out the more volatile products from the catalyst solution—the desired unsaturated compound or an ether and water, which often give low-boiling azeotropes. The reactor is heated by steam and the starting organic reagent is continually fed into the apparatus. Located above the reactor is a reflux condenser (sometimes a fractionating column), which is used to control the recycling of the condensate by maintaining the catalyst concentration constant.

The second method is employed for carrying out practically irreversible and sufficiently fast reactions of elimination of water with the formation of nitro-olefins, unsaturated aldehydes and ketones and other compounds. In this method, the acidified reagent is passed through a coil-type or tubular reactor at the required temperature.

Gas-phase dehydration is used for the production of styrene (from methylphenylcarbinol), isoprene (from isopentane-1,2-diols or isopentene-2), isobutylene (from *tert*-butanol), diethyl ether (from ethanol), tetrahydrofuran (from 1,4-butanediol), acetic anhydride (directly from acetic acid or via ketene) and other products. The most frequently used catalysts are phosphoric acid on porous inert supports, aluminium oxide and acid and neutral phosphates of calcium or manganese. The temperature ranges 225-250 °C (production of diethyl

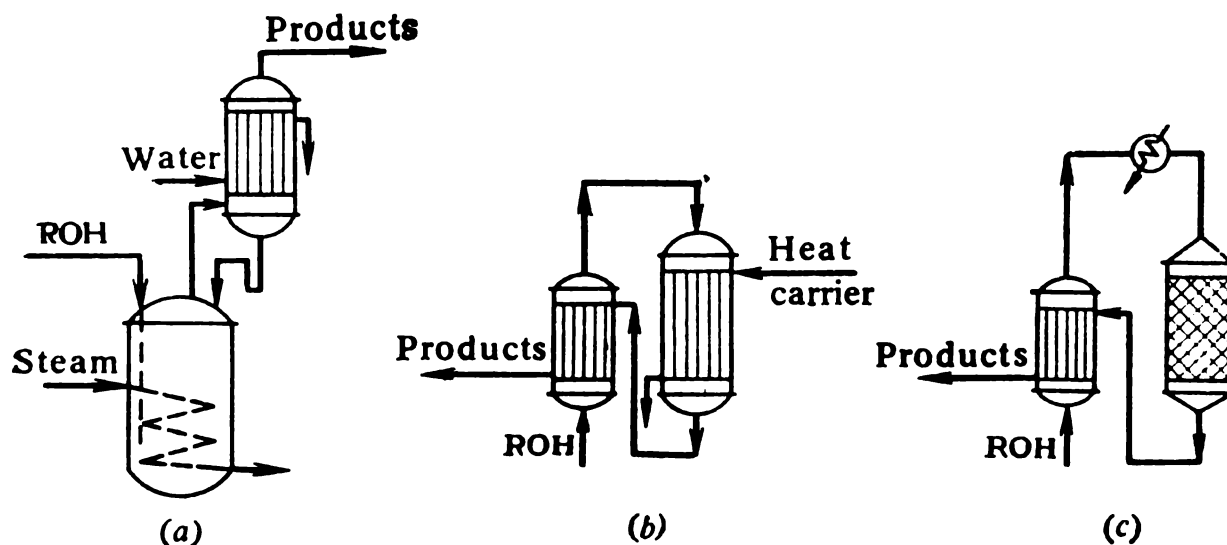


Fig. 3.11. Reaction units for dehydration processes:
a—liquid-phase process; b, c—gas-phase process.

ether) to 700-720 °C (the dehydration of acetic acid to ketene). The pressure is most often ordinary, but it may be 0.5-1 MPa for the production of diethyl ether and 0.02-0.03 MPa for dehydration to ketene.

Gas-phase dehydration is also accomplished by two principal methods. One is used for carrying out the endothermic processes of intramolecular dehydration. The reactor is a tubular vessel heated by a heat-exchange medium (see Fig. 3.11b) with a heterogeneous catalyst contained in its tubes. Because of the high metal capacity of these reactors, adiabatic reactors with a continuous bed of a heterogeneous catalyst and without a heat-exchange surface have found widest application (Fig. 3.11c). They are especially suited for carrying out the weakly exothermic reactions of ether formation with the temperature being easily controlled throughout the entire volume and maintained at an optimal level. In endothermic reactions of formation of unsaturated compounds, in order to maintain the required temperature regime the starting mixture is often diluted with superheated steam, which prevents the mixture from being strongly cooled and at the same time favours the increase of the reaction selectivity. Finally, there also exist plants with two adiabatic-type reactors connected in series: the gas cooled in the first

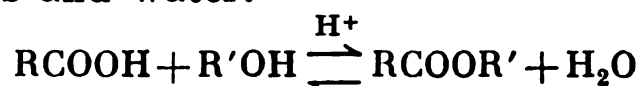
reactor is heated to the required temperature in a heat-exchanger with the aid of a suitable heat-exchange medium before being fed to the second reactor.

3.3. Esterification Processes

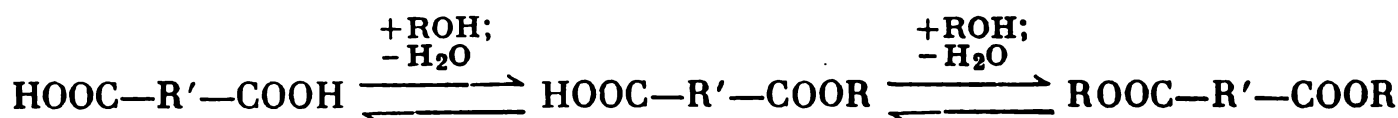
Broadly speaking, *esterification* reactions are processes leading to the formation of esters. Here we will be concerned only with the reactions of acids, their anhydrides and acid chlorides with alcohols and olefins and also with ester interchange reactions. These conversions are all of commercial importance.

3.3.1. Chemistry and Theoretical Foundations of Esterification Processes

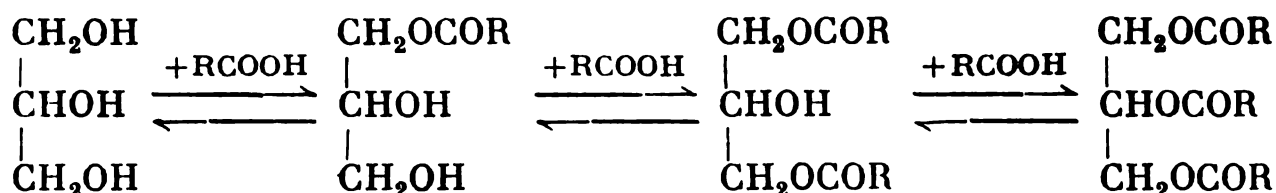
The most important esterification reaction is the reversible interaction of organic or inorganic acids with alcohols leading to the formation of esters and water:



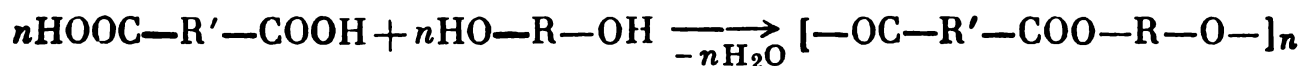
Dihydric alcohols give rise to two types of esters—acid esters and neutral esters, the yield of which depends on the ratio of the reactants:



In turn, dihydric and polyhydric alcohols can give rise to partial and full esters, this being also dependent on the ratio of the reactants used:



When both acid and alcohol are at least bifunctional, the process occurs with the formation of high-molecular-weight compounds, on which the synthesis of polyesters is based:



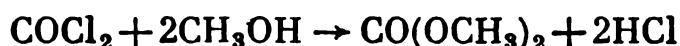
The reactions mentioned above are all equilibrium reactions, the reverse processes being the hydrolysis of esters, which is often called *saponification*.

The esterification of alcohols by carboxylic acids can be accomplished in the absence of catalysts, but in such a case it proceeds slowly

and for a sufficient reaction rate to be attained a high temperature (200-300 °C) is required. Still, when the catalyst impurity is difficult to wash off and it impairs the quality of the product, a non-catalytic process is operated.

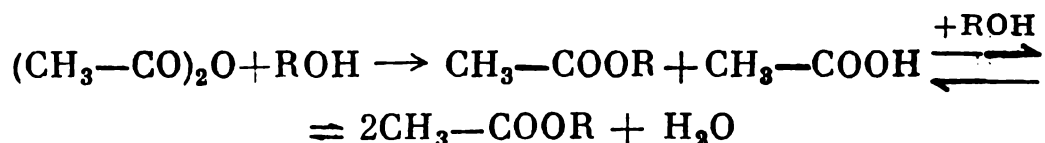
In the presence of acid catalysts (H_2SO_4 , HCl , arylsulphonic acids, ion-exchange resins) the esterification and hydrolysis of esters proceed at 70-150 °C. This method, which is carried out in the liquid phase, is a common method for the synthesis of the majority of esters. The catalysts used are also heterogeneous acid-type catalysts (Al_2O_3 , aluminosilicates, phosphates). In this case, esterification is conducted in the gas phase, but this method is employed relatively seldom.

In some cases, say for carbonic and phosphoric acids, the reaction with alcohols does not lead to the desired result, and in order to obtain esters of these acids, their acid chlorides are used:



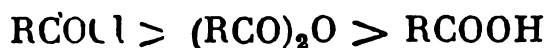
The acid chlorides of carboxylic acids are also suitable for esterification, but their use is limited because of the high cost of acid chlorides as compared with acids.

Acid chlorides may be replaced by acid anhydrides. Their reactions with alcohols proceed in two steps: an ester and an acid are first formed, and in a number of cases (say, the production of cellulose acetate) the process is completed. However, under more severe conditions, the acid liberated esterifies the alcohol according to the reversible reaction given above, both acyl groups of the anhydride being used:



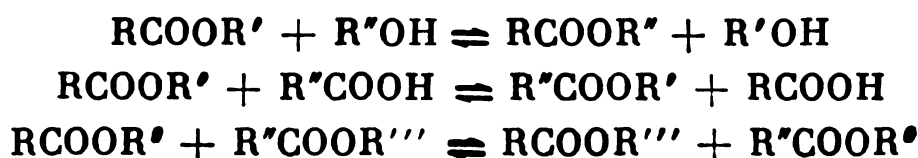
The first step occurs on slight heating and is speeded up by strong mineral acids. The second step is presumably analogous to the esterification effected by free acids and also requires acid-type catalysts. The esterification by acid anhydrides, which are usually more expensive than the acids themselves, also finds limited use, but it is widely employed when use is made of readily available cyclic anhydrides of dibasic acids (phthalic, maleic and other acids).

Of the esterifying agents listed above, the most active are acid chlorides, then come anhydrides, followed by the carboxylic acids themselves:



The class of reactions under consideration also includes the *alcoholysis* and *acidolysis* of esters and *transesterification* processes. They are all reactions involving the exchange decomposition of esters with

alcohols, acids or another ester:



The most important of these is the alcoholysis of esters, which is not infrequently used for industrial syntheses. Like the esterification by carboxylic acids, the alcoholysis, acidolysis and transesterification reactions are catalyzed by strong acids.

The direct esterification of carboxylic acids by olefins, in which the hydration of olefins is omitted, has lately come into use:



The reaction is also accelerated by acid catalysts.

Thermodynamics of Esterification Reactions. The interaction of alcohols with carboxylic acids in the liquid phase proceeds practically without absorption or evolution of heat ($\Delta H = 0$). Accordingly, alcoholysis, acidolysis and transesterification have also a heat effect close to zero. Hence, the equilibrium constants of these reactions do not depend on temperature. By contrast, the esterification of alcohols by acid chlorides of acids and also the first step of the esterification of alcohols by anhydrides are exothermic processes.

The reactions of carboxylic acids with alcohols are reversible, and despite the fact that the mixture is nonideal, the equilibrium is well described by the concentration equilibrium constant:

$$K_c = \frac{[\text{RCOOR}'] [\text{H}_2\text{O}]}{[\text{RCOOH}] [\text{R}'\text{OH}]}$$

The equilibrium constant depends on the structure of the acid and especially on the structure of the alcohol. For primary saturated alcohols with a straight chain the equilibrium constant of their liquid-phase esterification by acetic acid is 4-4.5 (with a stoichiometric amount of acid and alcohol in the starting mixture this corresponds to an equilibrium degree of conversion of 66-68 percent). An increase in the length of the carbon chain in the alcohol molecule leads to a certain decrease in the equilibrium constant. Secondary saturated alcohols and also allyl and benzyl alcohols are characterized by a lower equilibrium constant, from 2 to 2.5. The state of equilibrium is the least favourable in the esterification of tertiary alcohols and phenols: the equilibrium constants are very low—from 0.005 to 0.001, which with a stoichiometric ratio of the reactants gives an equilibrium degree of conversion of only 6-10 percent. As a result, tertiary alcohols and phenols are usually esterified by more active acid chlorides and anhydrides rather than by free acids.

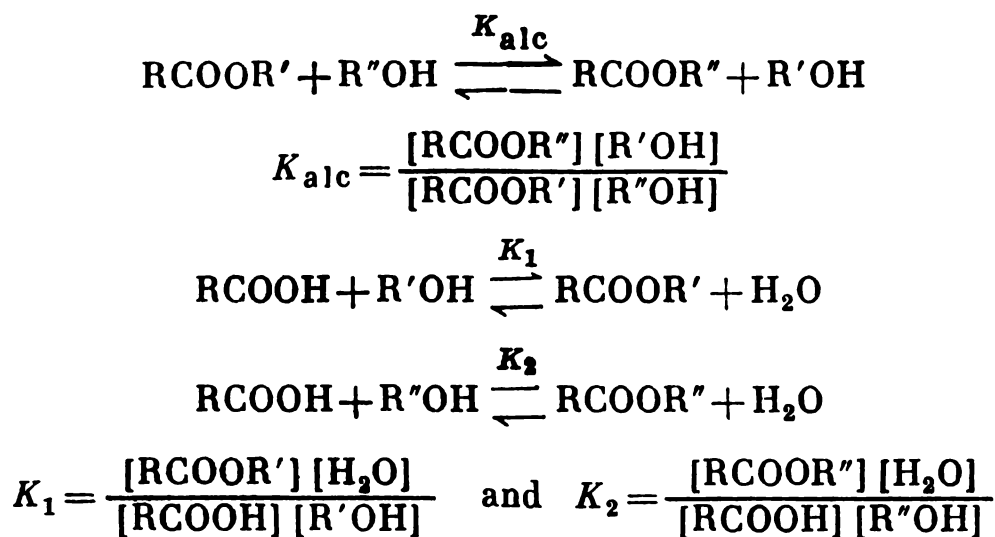
The effects of the structure of carboxylic acids on the equilibrium of esterification reactions is less pronounced and is opposite to the

effect of the structure of alcohols. The equilibrium constant increases with increasing length and degree of branching of the carbon chain in the acid molecule. For example, for trisubstituted acetic acids on interaction with primary saturated alcohols in the liquid phase it reaches 8-10, this being also observed for aromatic acids.

In contrast to the liquid-phase reactions, the gas-phase esterification of carboxylic acids with alcohols is an exothermic reaction and has a higher equilibrium constant, which depends on temperature. For instance, the equilibrium constant for the production of ethyl acetate in the gas phase is equal to 30 at 150 °C and to 9 at 300 °C.

There are several ways for increasing the degree of conversion of the reactants to esters. In liquid-phase reactions the most efficient way is to distill out water or ester as they are formed from the reaction mass. Where this cannot be done and also in all gas-phase esterification processes, the degree of conversion can be increased by taking an excess of one of the reactants, usually the cheapest one. In the reverse process—the hydrolysis of esters—other conditions are evidently required in order to raise the degree of conversion, namely the reaction must be carried out in excess water.

The position of equilibrium on alcoholysis, acidolysis and transesterification is governed by the equilibrium of the corresponding esterification processes. For example, in the alcoholysis and production of the same esters by esterification we have:



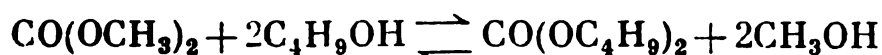
Dividing the last two expressions by each other, we obtain:

$$\frac{K_2}{K_1} = \frac{[\text{RCOOR}''] [\text{R}'\text{OH}]}{[\text{RCOOR}'] [\text{R}''\text{OH}]} = K_{\text{alc}}$$

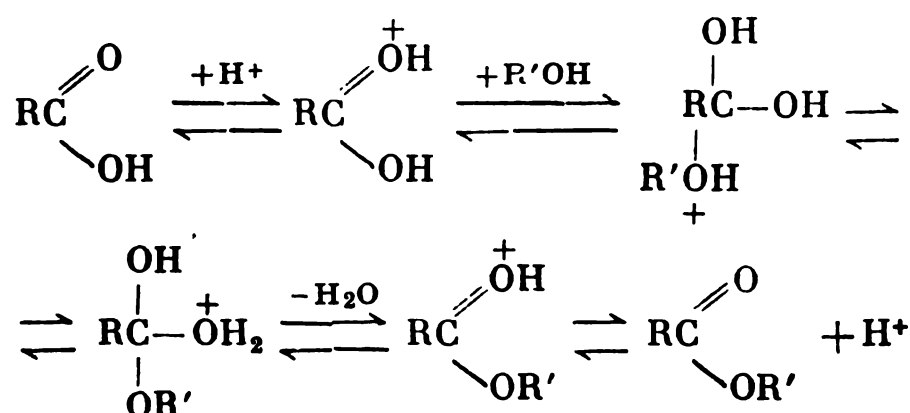
that is, the equilibrium constant for alcoholysis is equal to the quotient of division of the equilibrium constants of the corresponding esterification reactions. As a result, the equilibrium of alcoholysis reactions depends strongly on the structure of the alcoholic residue of the ester and on the structure of the alcohols that reacts with it. Obviously, the alcoholysis of ethyl esters by tertiary alcohols and

enols, for example, has a negligibly small equilibrium constant, so the reverse process will go almost to complete conversion.

The methods used to increase the degree of conversion for the alcoholysis of esters are analogous to those employed for esterification. The strongest effect is given by the removal of the alcohol from the reaction zone, when the alcoholysis is almost always carried out for the production of esters of higher-boiling alcohols; an example is



Mechanism and Kinetics of Esterification Reactions. In the majority of cases the esterification reaction proceeds by a bimolecular mechanism with the fission of the acyl-oxygen bond, when the slowest step is the attack of the protonated acid by the alcohol molecule:



All the steps are at equilibrium with the reverse reactions leading to the hydrolysis of the ester (or to the alcoholysis if an alcohol is taken instead of water).

The above mechanism is described by the following kinetic equation:

$$r = k_1 [\text{H}^+] \left\{ [\text{RCOOH}] [\text{R}'\text{OH}] - \frac{1}{K} [\text{RCOOR}'] [\text{H}_2\text{O}] \right\}$$

where k_1 is the rate constant of the forward reaction and K is the equilibrium constant. In practice, when the volatile reaction products (water or ester) are removed from the mixture, their concentration is decreased, and this concentration can be found only with account taken of the kinetics of mass transport. In noncatalytic esterification the order of the forward reaction with respect to the acid increases up to 1.5-2 according to data from different sources, which is ascribed to the autoprotolysis of the acid or by the fact that one of its molecules effects the acid catalysis of the process. This is described by the following kinetic equation:

$$r = k_1 [\text{RCOOH}]^{0.5-1} \left\{ [\text{RCOOH}] [\text{R}'\text{OH}] - \frac{1}{K} [\text{RCOOR}'] [\text{H}_2\text{O}] \right\}$$

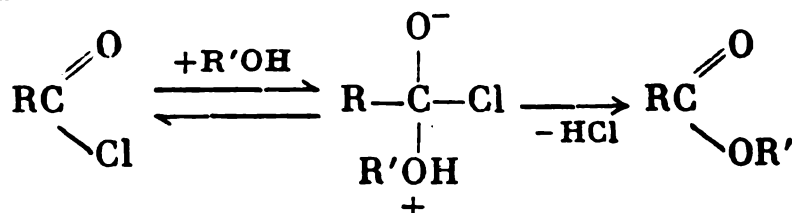
The mechanism of the esterification of alcohols with anhydrides upon acid catalysis is analogous to that described above. The pro-

process distinctly splits into two steps (Fig. 3.12): the fast reaction of alcohol with anhydride described by the following kinetic equation

$$r = k[H^+][(RCO)_2O][R'OH]$$

and the slow esterification of the carboxylic acid formed, for which the first of the equation given above is valid.

In the esterification with acid chlorides either there is no acid catalysis or it is weakly pronounced. The bimolecular mechanism of the reaction



is described by the following second-order kinetic equation:

$$r = k[\text{RCOCl}][\text{R}'\text{OH}]$$

The dependence of the reactivity of the acid and alcohol components on their structure is the same for the esterification with acids

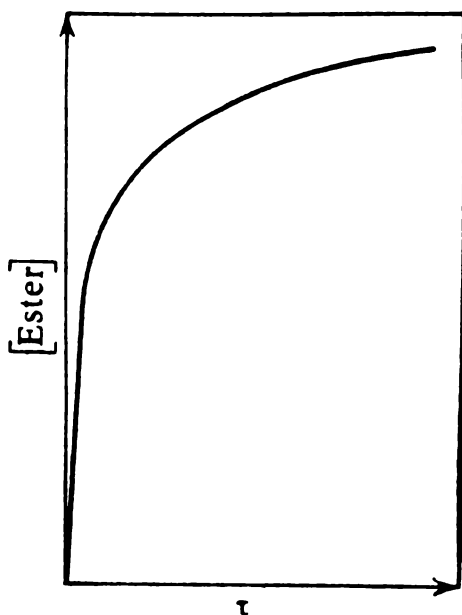


Fig. 3.12. Dependence of the ester concentration in the esterification of alcohol by acid anhydride on the reaction time.

anhydrides and acid chlorides. The structure of the alcohol has the same effect on the rate of the reaction as it has on its equilibrium, i.e., the reaction rate decreases with increasing chain length and degree of branching of the alkyl group. The esterification of tertiary alcohols and phenols proceeds especially slowly—for these the reaction velocity is about 100 times slower than for primary alcohols. Secondary alcoholic groups are esterified at a rate 6-10 times slower than the primary groups.

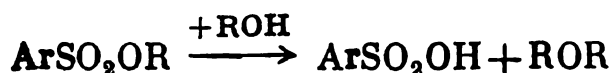
The structural changes in the molecule of a carboxylic acid have an opposite effect on the rate of esterification as compared with their

effect on the reaction equilibrium. For example, an increase in the length and degree of branching of the carbon chain, which, as we have seen above, leads to an increase in the equilibrium constant, lowers the reaction velocity. Trisubstituted acetic and aromatic acids react especially slowly: the rate of their esterification is 40-100 times slower than for acetic acid. Conversely, formic acid has the highest reactivity.

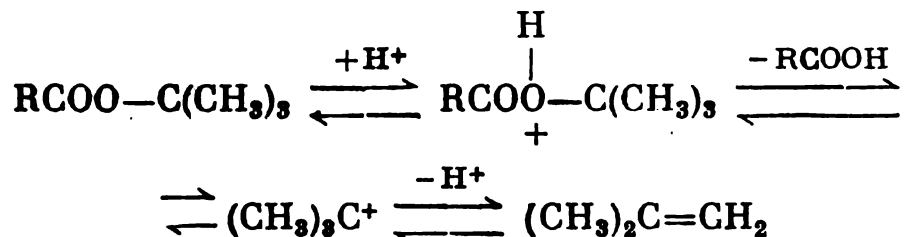
In the case of polybasic acids or their acid chlorides the first functional group reacts more rapidly than the succeeding ones but they are separated by a sufficiently long carbon chain, this difference becomes small. For this reason, this phenomenon is especially strongly pronounced for polybasic acids and acid chlorides, in which all the functional groups are attached to one atom (H_2SO_4 , Cl_2 , POCl_3). For them the difference in reactivity upon successive esterification is so large that each of the steps can be sharply separated by choosing reaction conditions and by proportioning the amount of alcohol to be used:



Reactions at the Alkyl-Oxygen Bond and Direct Synthesis of Esters from Olefins. Apart from the above-described reactions taking place at the acyl-oxygen bond, which are typical of ester-formation and ester-interchange reactions, there are also possible processes which involve the formation or fission of alkyl-oxygen bonds. These reactions not infrequently proceed through the intermediate formation of carbonium ions and are favoured by the structure of the alcoholic and acidic components that favours the polarization of the alkyl-oxygen bond or the stabilization of the carbonium ion. Owing to this property, some esters, especially the esters of sulphuric acid and arylsulphonic acids, are known to be strong alkylating agents:



and ethers are sometimes the by-products of esterification reactions. With carboxylic acids, such properties are displayed more strongly by esters of tertiary alcohols, whose synthesis and conversions lead to the formation of by-product isoolefins:

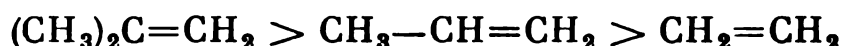


The direct synthesis of esters from carboxylic acids and olefins is based on the reverse direction of this process. The reaction is exothermic and reversible, and its thermodynamic characteristics can be calculated from the sequence of the processes of olefin hydration and alcohol esterification:



The equilibrium constant of the overall reaction is equal to the product of the equilibrium constants of hydration and esterification and

is, other conditions being equal, the lowest for isoolefins and, hence, for the esters of tertiary alcohols. On the other hand, the reactivity of olefins depends on the stability of intermediate carbonium ions and increases in the following order:



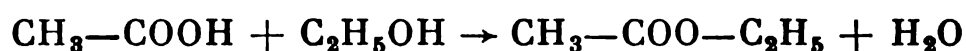
For slightly reactive ethylene too high a temperature is required when the equilibrium is unfavourable for the process. Therefore the reaction is most suitable for propylene and its homologues.

3.3.2. Technology of the Synthesis of Esters of Carboxylic Acids

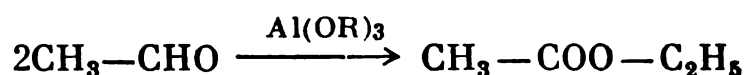
The esters of carboxylic acids are of practical importance as solvents, hydraulic brake fluids, lubricating oils, plasticizers and monomers.

The esters used as solvents are those of less expensive and more available acids and alcohols, primarily the esters of acetic acid with lower alcohols. These esters are all colourless and slightly soluble in water. Their shortcomings are high flammability and explosiveness.

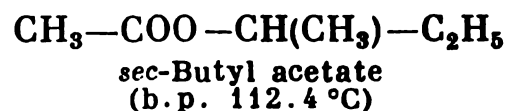
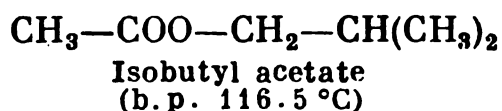
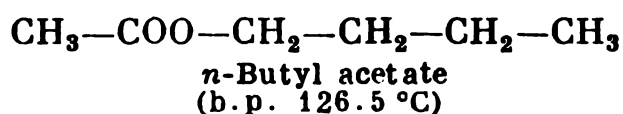
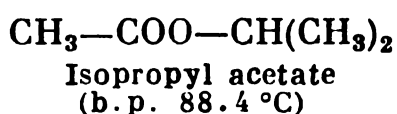
Ethyl acetate, $\text{CH}_3-\text{COO}-\text{C}_2\text{H}_5$ (b.p. 77.1°C) is made by the esterification of ethyl alcohol with acetic acid:



Another method, which has also been realized on an industrial scale, is to convert acetaldehyde according to the Tishchenko reaction using aluminium ethoxide as catalyst:



The esters of acetic acid with monohydric alcohols—the homologues of ethanol—are also of practical value; they are obtained by the esterification of the corresponding alcohols by acetic acid. Of these, mention should be made of the following esters:



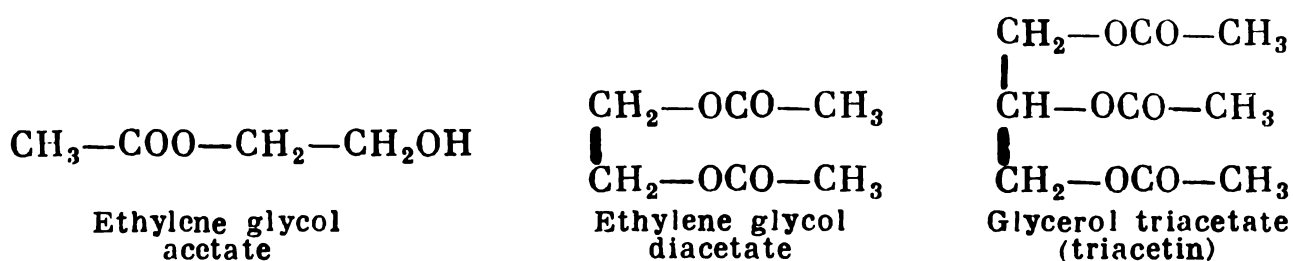
and technical *amyl acetate*, $\text{CH}_3-\text{COO}-\text{C}_5\text{H}_{11}$, which is a mixture of the esters of amyl alcohols obtained by the hydrolysis of a mixture of chloropentanes.

Isopropyl and *sec*-butyl acetates are currently manufactured by a more efficient method of direct synthesis from propylene or *n*-bu-

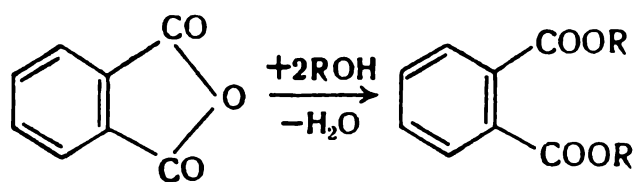
ylene and acetic acid:



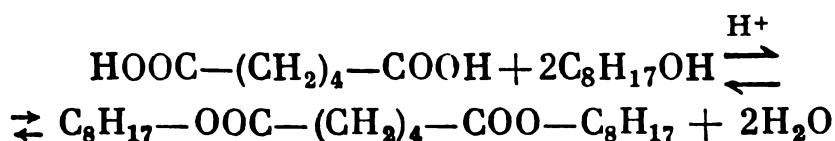
The esters of acetic acid with polyhydric alcohols, such as ethylene glycol and glycerol, are also employed as solvents:



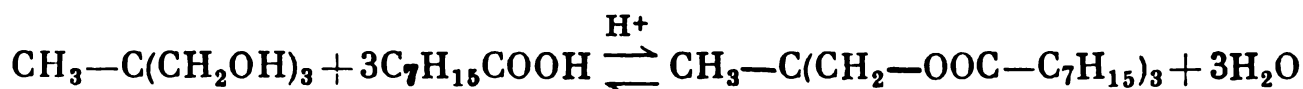
Of most importance as plasticizers are the esters of phthalic acid which are obtained from phthalic anhydride and C_4 - C_8 alcohols, specially from isooctyl and 2-ethylhexyl alcohols:



The corresponding esters of isophthalic (*m*-benzenedicarboxylic) acid are used for the same purpose. In many cases, the esters used as plasticizers are identical in composition to those used as lubricating oils. Examples are the full esters of dibasic aliphatic acids (adipic, methyladipic and sebacic acids) with higher monohydric alcohols (*n*-octyl, iso-octyl, 2-ethylhexyl, isononyl, and isodecyl alcohols, and butyl cellosolve). They are produced by the esterification of alcohols with acids in the presence of acid catalysts:



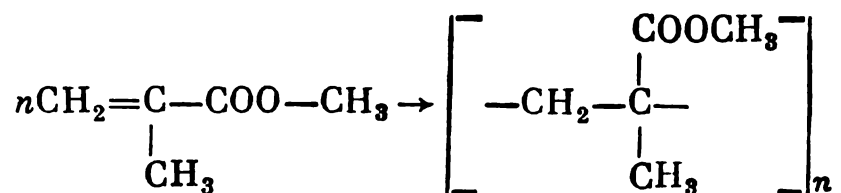
The esters used as plasticizers and lubricating oils also include the full esters of di-, tri- and polyethylene glycols, $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, pentaerythritol, $\text{C}(\text{CH}_2\text{OH})_4$, trimethylolethane, $\text{CH}_3\text{C}(\text{CH}_2\text{OH})_3$, trimethylolpropane, $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{OH})_3$, and higher monobasic C_6 - C_9 acids. These full esters are made by ordinary esterification:



In this way there are also obtained the esters of α, α' -branched neoacids, $\text{R}(\text{CH}_3)_2\text{C}-\text{COOR}$, which are noted for high stability towards hydrolysis and other chemical conversions.

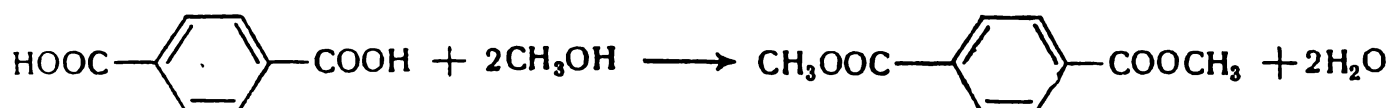
The esters of unsaturated acids with alcohols are capable of polymerization with the formation of valuable products owing to the presence of double bonds. Of importance are the esters of acrylic and methacrylic acids, especially *methyl methacrylate*,

$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$ (b.p. 100.3°C). Upon polymerization it gives *polymethyl methacrylate* (organic glass or Plexiglas):

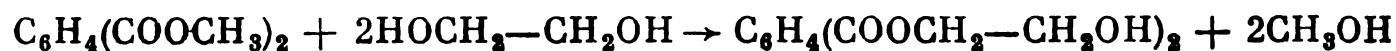


which is widely used for the fabrication of domestic and technical articles. The esters of acrylic acid, $\text{CH}_2=\text{CH}-\text{COOR}$, form polymers having a low softening temperature, which is why their outlets are as copolymers.

Polyethylene terephthalate, which is used for the manufacture of an important synthetic fibre (Terylene, Dacron or Lavan), is produced by using the *dimethyl ester of terephthalic acid* (b.p. $140\text{--}141^\circ\text{C}$):



The polymer is obtained by subjecting dimethyl terephthalate to alcoholysis by ethylene glycol:



and then to polycondensation.

The esters of allyl alcohol, say diallyl phthalate, are used as monomers on a minor scale. Vinyl esters are not considered here because they are obtained by methods other than esterification reactions.

3.3.2.1. Technology of Esterification Processes

The technological processes of synthesis of esters may be classified into two principal groups: (1) liquid-phase processes—noncatalytic or homogeneous-catalytic processes, in which the chemical reaction is combined to varying extents with the separation process; (2) heterogeneous-catalytic reactions in the liquid or gas phase, which are carried out in continuous-flow vessels separately from the separation processes.

Processes of the first group are traditional and are the most popular in esterification technology. These processes are designed so as to carry out as completely as possible the reversible synthesis of an ester by shifting the equilibrium due to the distillation of volatile products (water, an ester or their azeotropic mixture). In this respect, acids, alcohols and their esters are divided into four types:

1. The high-boiling esters of slightly volatile acids and alcohols. These include the esters of dibasic acids (phthalic, sebacic, and adipic) and also those of monocarboxylic $\text{C}_4\text{--}\text{C}_5$ and higher acids with

glycols, glycerol, or higher monohydric alcohols. The most volatile component of such a mixture is water, which is distilled out as it is formed with no appreciable impurity of the reagent or ester. In order to facilitate the evaporation of water, either the reaction mass may be purged by an inert gas or the distillation carried out in vacuum.

2. The high-boiling esters of sufficiently volatile acids and alcohols. In the preparation of the esters of higher acids with C_1 - C_8 alcohols and also of the esters of acetic and formic acids with glycols and glycerol, the water is distilled out of the reaction mass together with the volatile reagent. Butyl and higher alcohols form with water azeotropic mixtures, which on condensation are separated into two layers. By recycling the alcohol to the reaction and removing the aqueous (lower) layer, it is possible to attain a high degree of conversion. When the condensate is homogeneous, certain compounds (benzene or dichloroethane) are added sometimes; with water these compounds give azeotropes. The water is removed together with these compounds, and the azeotropic component added is recycled to the reactor after the condensation of the vapours and separation from the water. This operation is not suitable for the production of the esters of methyl and ethyl alcohols: the water is distilled out together with excess alcohol and the aqueous alcohol is then subjected to fractionation.

3. Esters of medium volatility which form with water (or with water and alcohol) azeotropic mixtures, in which water predominates over the ester in the molar ratio. Such esters include butyl and amyl acetates. The lowest-boiling of the azeotropic mixtures formed in these systems consists of ester, alcohol and water. In the case of butyl acetate the mixture contains 35.5 percent (by weight) of ester and 37.3 percent (by weight) of water, which is equivalent to their molar ratio of about 1 : 7. This means that a large amount of water is removed together with the azeotropic mixture and the reaction mass is continually enriched with the ester. When the distilled vapours are condensed, two layers are formed—an aqueous layer and an organic layer. The latter contains ester and alcohol, which are returned to the reactor.

4. Highly volatile esters, which give with alcohol and water ternary azeotropes, in which the ester predominates over water in the molar ratio. For example, ethyl acetate, ethyl alcohol and water form an azeotropic mixture (b.p. 70.3 °C) containing 83.2 percent (by weight) of ester and 7.8 percent (by weight) of water, which corresponds to their molar ratio of 2.4 : 1. When such a mixture is distilled off, the reaction mass becomes increasingly enriched with water. Thus, here the ester is obtained in the form of a distillate taken off from the reactor together with a certain amount of water and alcohol.

Since the volatile material is distilled out, the reagents may be used in a ratio close to the stoichiometric ratio, but when full esters are produced, the tendency is to attain a high degree of conversion of the acid by using an excess of alcohol, which depends on the amount carried over by the reaction product distilled off. The amount of the catalyst is about 0.1 percent, which allows the process to be accomplished in 2-6 hours. In the noncatalytic reaction the same reaction time is attained through the use of higher temperatures.

The esterification process combined with the distillation of the azeotropic mixture can be operated either batchwise or continuously;

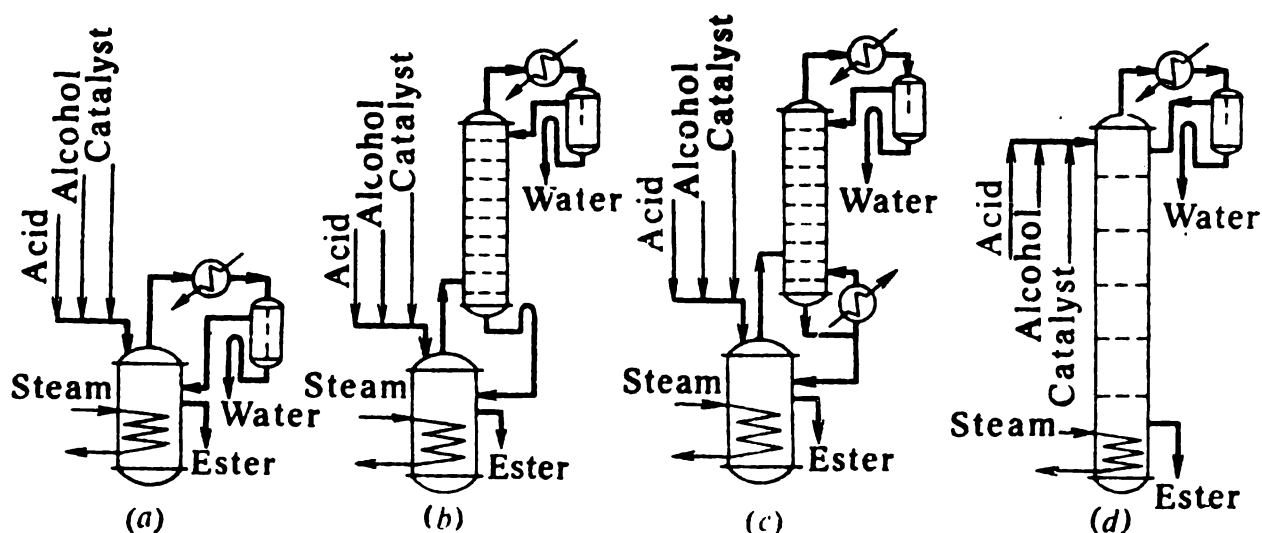


Fig. 3.13. Reaction units for liquid-phase esterification processes combined with the distillation of the azeotropic mixture:

a—still with a condenser; *b*—still with a dephlegmating column; *c*—still with a fractionating column; *d*—reactor of the tray-column type.

the continuous operation is more common. The principal reaction units employed for the continuous esterification process are shown in Fig. 3.13.

The first three esterifying reactors have a sufficiently large volume; they are heated by steam through the jacket or by coils. The liquid in the reactor is in boiling state (or the volatile component is evaporating from it). The chemical conversion occurs when the reagents are continually fed into the reactor and the volatile product is distilled off. The units *a*, *b* and *c* differ only by the efficiency of the separation systems: the first is equipped only with a reflux condenser, the second with a dephlegmating column and the third with a fractionating column and a boiler, which makes it possible to increase the reflux ratio and the separation efficiency. It is expedient to use these systems, respectively, at a large, medium or small difference in the volatility of the still liquid left in the reactor and of the distillate taken from the reaction mass. These three systems are also suitable for the similar cases in batch esterification processes; the flow diagrams are given for systems, in which the ester is left in the still and the volatile constituent is an azeotropic mixture of

water and ester, which is split in separators into two layers (the water is removed from the system).

In the continuous esterification process, the stills *a*, *b* and *c* will operate satisfactorily only with the chemical reaction proceeding at a high velocity, otherwise the conversion or reactor capacity will be too low. Therefore, the continuous operations are carried out using a series (a cascade) of esterifying columns with the overflow of the still liquid from one reactor into another, each esterifying reactor being equipped with an appropriate separation system.

Another variant consists of the use of an esterifying reactor of the tray-column type (Fig. 3.13*d*). Each of the trays with a liquid layer 0.5-1 m high serves as a separate reactor; the liquid overflows in the column from top to bottom and is in a state of boiling at each tray, which makes it possible to combine the chemical reaction with fractionation. The catalyst and the less volatile reagent (usually the acid) are fed to one of the upper trays, and the second reagent is introduced at a definite point along the height of the column corresponding to the volatility of the reagent, the liquid and the vapour moving countercurrently to each other. Such a unit is especially suitable for relatively slow chemical reactions (typical of esterification with a low catalyst concentration) and with a small difference between the volatility of the distillate and that of the still residue.

As a typical example, we will consider the flow diagram of the continuous production of a low-boiling ester, ethyl acetate, shown in Fig. 3.14.

The starting mixture of the reagents containing acetic acid, ethyl alcohol and sulphuric acid as the catalyst is continually fed from pressure tank 1 to the reactor through the flow meter. First it passes through heat exchanger 2, where it is heated by the vapours leaving the reaction column and then is fed to the upper tray of esterifying column 4. As a result of the column still being heated by live steam, the ethyl acetate formed is distilled out together with the alcohol and water vapours from the column and the liquid becomes enriched with water while flowing downwards through the trays. The residence time of the reaction mass in the esterifying reactor and the ratio of the reagents are chosen so that the still liquid contains a small amount of unchanged acetic acid (all of the sulphuric acid is also left in it). This liquid is withdrawn from the still to waste after being neutralized.

The vapours leaving the top of the reactor contains about 70 percent of alcohol and 20 percent of ester. They are sent for cooling and condensation first to heat exchanger 2, where the mixture of the starting reactants is heated, and then to condenser 3. The condensate from unit 2 and part of the condensate from apparatus 3 are returned to the top tray of reactor 4. The remainder passes into fractionating column 5 designed for the separation

of the azeotropic mixture from the aqueous alcohol. The column still is fitted with a coil for heating by indirect steam and the reflux is generated in apparatus 6, from which part of the condensate is returned to refluxing. The still liquid of column 5 consists of alcohol (the greater part) and water. It is removed from the column and sent to one of the lower trays of esterifying reactor 4 in order to provide a sufficient amount of alcohol in the lower section of this column and to attain a more complete conversion of acetic acid.

The vapours from column 5 are condensed in unit 6, from which part of the condensate passes to refluxing, the remainder being

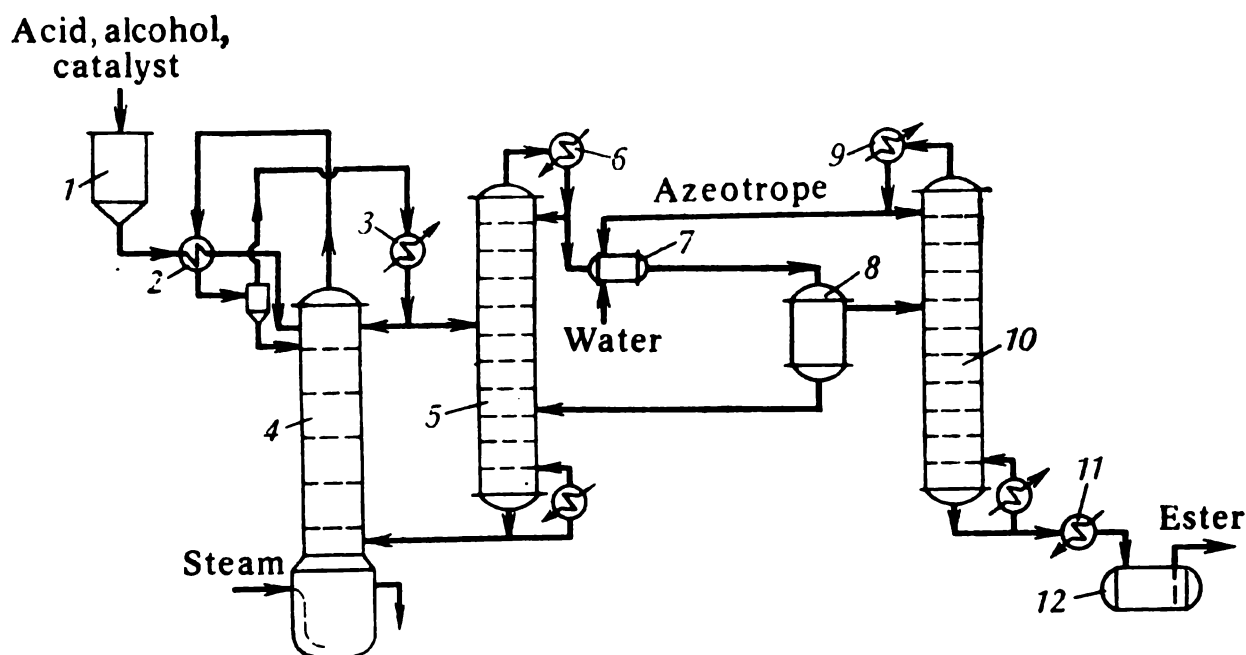


Fig. 3.14. Flow diagram of continuous production of ethyl acetate:

1—pressure tank; 2—heat exchanger; 3—condenser; 4—esterifying column; 5, 10—fractionating columns; 6, 9—condenser-dephlegmators; 7—mixer; 8—separator; 11—cooler; 12—ethyl-acetate collector.

sent to mixer 7, where it is diluted with about the same amount of water (otherwise the condensate will not separate into layers because water dissolves well in an ester-alcohol mixture). The emulsion formed is separated in continuous-action separator 8 into two layers—the upper layer containing the ester with the dissolved alcohol and water, and the lower layer, which is an aqueous solution of alcohol and ester. The lower layer is returned to one of the middle trays of column 5.

The crude ester from separator 8 is sent for purification from water and alcohol. The purification is effected in fractionating column 10 by distilling out the low-boiling ternary azeotrope of ester, alcohol and water. Part of this mixture leaves condenser 9 and passes to column 10 to reflux, the remainder being returned to mixer 7. Ethyl acetate from the still of column 10 is sent to collector 12 after being chilled in cooler 11.

Some esters are produced by the process substantially different from that described above. For example, dimethyl terephthalate is made from high-melting and difficultly soluble terephthalic acid and methyl alcohol under pressure at 250-270 °C with no catalyst present (in order to avoid the gum formation in the product and provide the subsequent purification from the catalyst). The reactor is a vessel equipped with a stirrer, from which the mixture of ester, excess methanol and water is sent for separation, the methanol being recycled.

In the production of dialkylphthalate plasticizers from phthalic anhydride and C_4 - C_8 alcohols the nature of the catalyst plays an important role. The use of acids leads for the neutralization and washing of the product and causes a darkening of the product, which impairs its usage properties. This has led to the replacement of acids by TiO_2 and $Sn(OR)_4$.

The process is operated batchwise or continuously in two steps: the first, fast reaction, in which one alkyl group is introduced, is carried out in a stirred reactor, into which the alcohol and solid or preliminarily melted phthalic anhydride are added. The second, slow step is conducted in an esterifying reactor of the tray-column type (see Fig. 3.13d). In such cases, for octyl esters to be synthesized, a foreign azeotrope source is sometimes recommended; no such azeotrope source is present in other schemes, the water being distilled out as an azeotrope with an excess of octyl alcohols.

Esterification Effected by Heterogeneous Catalysis. On catalysis using protic acids the product must be neutralized. In most cases, the ester is left in the still and after the acid is neutralized the ester must be washed, etc. This results in an increased consumption of the reagents, a loss of the ester and the formation of waste waters. It is for these reasons that the heterogeneous catalysis of esterification reactions has recently found wide application, especially the catalysis using sulphonic cation-exchangers at a synthesis temperature of up to 150-160 °C.

The esterification catalyzed by sulphonic cation-exchangers is carried out in a column-type reactor with a continuous catalyst

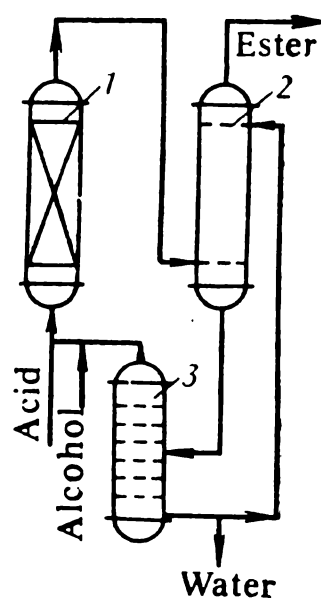


Fig. 3.15. Flow diagram for esterification catalyzed by a sulphonic cation exchanger:

1—reactor; 2—extraction column; 3—alcohol recovery column.

bed, since the absence of the reaction heat makes heat-exchangers useless. The reaction proceeds in the liquid phase, an excess of alcohol is used for the synthesis of esters of lower alcohols in order to increase the degree of conversion of the acid. One of the possible flow diagrams (Fig. 3.15) is realized by using an adiabatic reactor containing a packing of a sulphonic cation-exchanger, an extraction column, in which excess alcohol (and the unchanged acid) is absorbed by water from the reaction mass, and a stripping column, where the alcohol is distilled out and recycled to the reaction. The water supplied to the extraction stage is also recycled; only a small amount of the reaction water is withdrawn from the system after the unconverted acid is recovered from it. The crude ester leaving the top of the extraction column is purified by fractional distillation.

The synthesis of esters from olefins is also possible by catalysis using sulphonic cation-exchangers. For instance, *sec*-butyl acetate is produced from *n*-butylene and acetic acid at 110-120 °C and a pressure of 1.5-2.5 MPa by using a sulphonic cation-exchanger having a selectivity of 100 percent. In this case, heterogeneous acid-type catalysts may also be used, with the two reagents being in the vapour phase. For example, isopropyl acetate is made from propylene and acetic acid at 120-160 °C under a pressure of 0.7-1.2 MPa, with a selectivity of 100 percent.

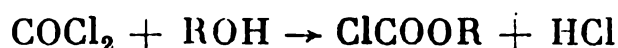
3.3.3. Production of Esters from Acid Chlorides. Carbonates and Esters of Phosphorus Acids

The esters of carboxylic acids are very seldom obtained from acid chlorides since the latter are expensive compounds. By contrast, the esters of carbonic acid (carbonates) and those of phosphorus acids are largely synthesized from acid chlorides since the corresponding acids are not capable of esterification.

3.3.3.1. Synthesis of Chlorocarbonates and Carbonates

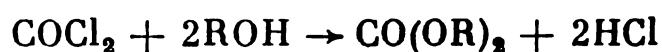
These esters are obtained from phosgene (carbonyl chloride), COCl_2 , which is the acid chloride of carbonic acid (H_2CO_3). Under normal conditions phosgene is a gas which is condensed to a liquid at +8 °C. The reaction occurs by way of the substitution of an alkoxy group for chlorine atoms in the absence of catalysts. Both chlorine atoms are replaced, the first of them rapidly and the second much more slowly. This makes it possible to obtain chlorocarbonic esters (*chlorocarbonates*) in high yield at a lower temperature and with a molar ratio of the reactants of 1 : 1. According to another classification, chlorocarbonates are also known as *chloroformates*,

i.e., the esters of chloroformic acid:



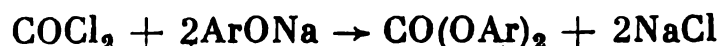
Apart from the temperature and the molar ratio of the reagents, the high yield of chlorocarbonates is also favoured by the order in which the reagents are charged into the reactor: alcohol must be added to an excess of phosgene. Thus, in batch operations the synthesis of chlorocarbonates is carried out on cooling (down to about 0 °C) and agitation, the required amount of alcohol being added to the liquid phosgene. The product is purged from the dissolved HCl and the liberated HCl is purified from phosgene and used in the form of hydrochloric acid. Chlorocarbonates are of great practical value for the production of pesticides—the esters of carbamic acids (carbamates), RNHCOOR .

The diesters of carbonic acid (carbonates) are produced from phosgene at 70-100 °C and a small excess of alcohol:



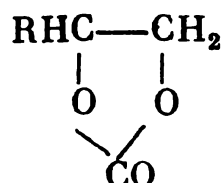
The side reaction consists of the formation of an alkyl chloride from alcohol and HCl. If the side reaction is substantial, the HCl formed can be bound by dry soda, calcium carbonate or a tertiary amine.

In the production of phenol esters, which are less reactive than alcohols, the reaction is effected with aqueous solutions of phenates (phenolates):

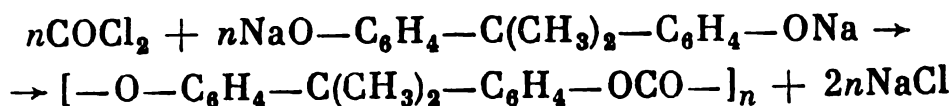


In order to avoid the side hydrolysis of phosgene, the process is carried out here with using a sufficiently concentrated solution of the phenate and in the presence of free phenol (in order to lower the concentration of hydroxyl ions).

Of the diesters of carbonic acid, the cyclic carbonates of glycols are of prime importance:

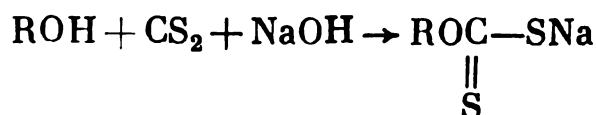


These cyclic carbonates are valuable solvents; the polycarbonates obtained from phosgene and an alkaline solution of certain bisphenols, especially diphenylolpropane, are valuable polymers:

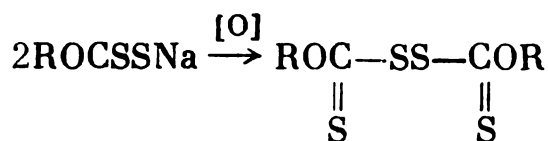


Mention should also be made of the esters of dithiocarbonic acid (*xanthates*). The salts of alkyl xanthates are produced from alcoholic

alkali and carbon disulphide (the anhydride of dithiocarbonic acid):



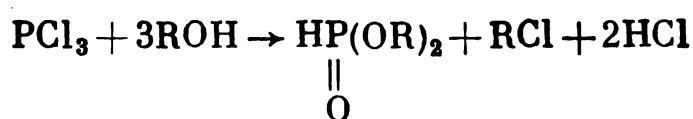
Sodium isopropylxanthate is used as an effective herbicide. Some xanthate disulphides produced by the oxidation of alkyl xanthates are also effective herbicides:



3.3.3.2. Esters of Phosphorus Acids

There are many esters of phosphorus acids, but here we shall be concerned only with the most important esters. They are produced from phosphorus trichloride (PCl_3), phosphoric oxychloride (POCl_3) and phosphorus thiotrichloride (PSCl_3). The reactivity of these acid chlorides towards alcohols and phenols varies in the following order: $\text{PCl}_3 > \text{POCl}_3 > \text{PSCl}_3$; just as with phosgene, the replacement of each of the succeeding chlorine atoms occurs more and more slowly. This allows the synthesis of partial, full and mixed (with different alcohols) esters.

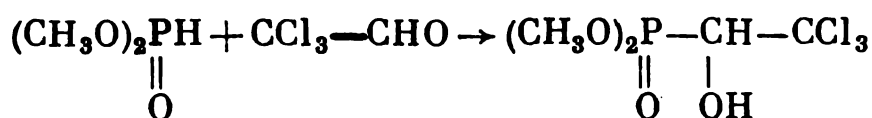
Reactions of PCl_3 with Alcohols. These reactions proceed even at low temperatures very vigorously and with the evolution of a large amount of heat. The substitution is accompanied by an Arbuzov rearrangement, the compounds formed being a dialkyl phosphite and an alkyl chloride:



This route is most often employed to produce *dimethyl phosphite*, $\text{HPO}(\text{OCH}_3)_2$. This compound is synthesized (either batchwise or continuously) in a solution of liquid methyl chloride at -24°C . The heat of reaction is removed by evaporation of the solvent, part of which is purified and sold as a commercial product. The hydrogen chloride formed is recovered in the form of 20-30-percent hydrochloric acid. The dimethyl phosphite is purified in a film evaporator by vacuum distillation.

Dimethyl phosphite is an intermediate for the synthesis of other phosphorus-containing compounds. For example, it is the starting material for the well-known insecticide *Trichlorfon* (*Dipterex*), known as *chlorophos* in the USSR, which is a derivative of alkylphosphonic acid. For this purpose, dimethyl phosphite is condensed with chloral

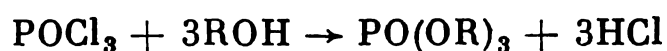
cooling:



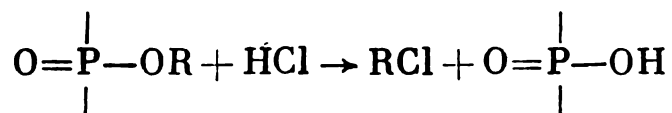
A single-step process has been proposed, in which the synthesis of dimethyl phosphite from CH_3OH and PCl_3 is combined with the synthesis of Trichlorfon from dimethyl phosphite and chloral.

Reactions of POCl_3 with Alcohols and Phenols. These reactions are of value chiefly for the synthesis of extractants (tributyl phosphate), plasticizers (tricresyl phosphate, etc.) and fire-resistant compounds.

The interaction of phosphoric oxychloride with alcohols occurs in the absence of catalysts and alkalis on cooling; heating is required only when the last chlorine atom is to be replaced:

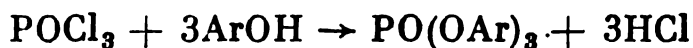


order to avoid the formation of by-product alkyl chlorides.



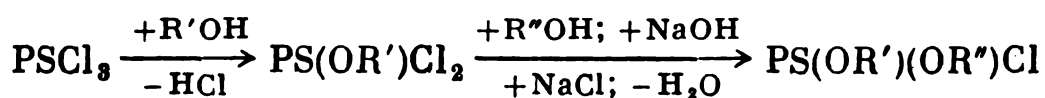
HCl must be purged in the current of an inert gas.

phenols, which are less reactive, interact with phosphoric oxychloride on heating and in the presence of catalysts—anhydrous ZnCl_2 , CaCl_2 .



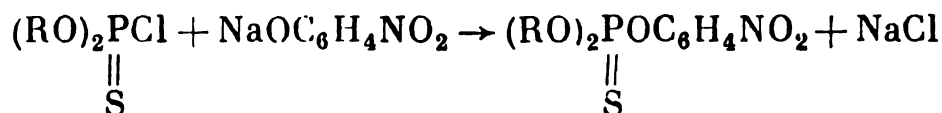
hydrogen chloride is allowed to vaporize from the reaction mixture and it is recovered in the form of concentrated hydrochloric acid. This process (operated batchwise or continuously) is used on a large scale to produce tricresyl phosphate—a plasticizer for polymeric materials.

Reactions of PSCl_3 with Alcohols and Phenols. These reactions are exclusively employed for the synthesis of pesticides. The first chlorine atom is replaced under the influence of alcohols at 20-30°C; for the second chlorine atom to be replaced, an alcoholic solution of alkali is needed; the third chlorine atom is replaced through the interaction with an alcoholate (alkoxide) or phenolate. In the synthesis of most pesticides of this series the first stage is the preparation of dialkyl chlorothiophosphates having identical or different alkyl groups (usually with a methyl or ethyl group):



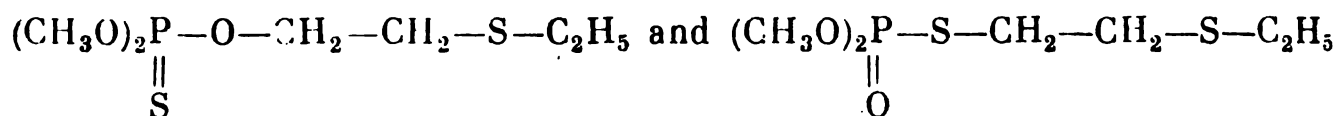
The pesticides *metaphos* (methyl parathion) and *thiophos* (parathion) are then produced, respectively, from dimethyl and diethyl

chlorothiophosphates and sodium *n*-nitrophenate:



Best results are obtained when the reaction is carried out in a medium of acetone or methyl ethyl ketone; both reagents are well homogenized. The process can, however, be also effected with an aqueous solution of nitrophenate with a dialkyl chlorothiophosphate being added to it at 50-100 °C. In order to avoid side hydrolysis, the pH of the medium must be controlled so as to provide an excess of free phenol.

In an analogous way, the insecticide *methylmercaptophos* is obtained from dimethyl chlorothiophosphate and β -hydroxydiethyl sulphide. *methylmercaptophos* is partially isomerized to a thiol derivative and is a mixture of two compounds:



3.4. Synthesis and Conversions of Nitrogen Derivatives of Acids

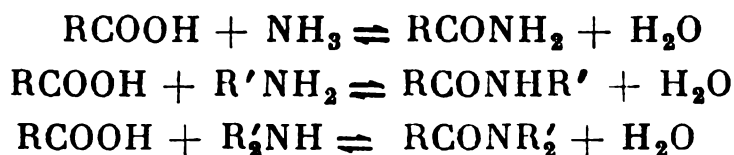
Here we shall consider two groups of processes that have direct relation to hydration, dehydration and esterification reactions:

1. The synthesis of nitrogen derivatives of carboxylic acids, the hydration, dehydration and esterification.
2. The synthesis of nitrogen derivatives of carbonic acid (isocyanates, substituted carbamides, carbamates, etc.).

3.4.1. Synthesis and Conversions of Nitrogen Derivatives of Carboxylic Acids

3.4.1.1. Amidation

The interaction of ammonia, and primary or secondary amines with carboxylic acids leads to acid amides:



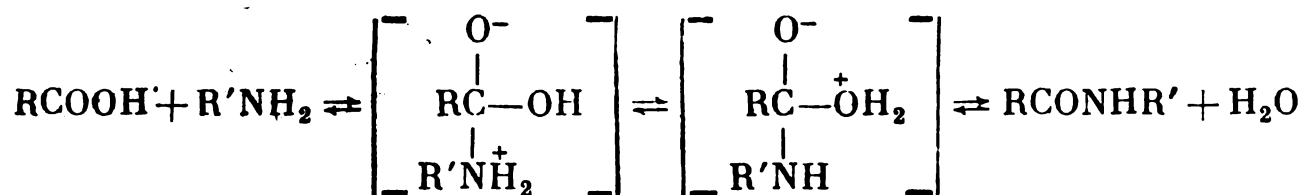
The reaction is in many respects similar to esterification. It is also reversible, but as compared with esterification its equilibrium is more strongly shifted to the right. The structure of the acid has the same effect on the thermodynamics and rate of amidation as

the case of esterification (branching and lengthening of the carbon chain of the acid increase the equilibrium constant but decrease the rate of the process). Ammonia and especially amines are stronger nucleophilic reagents than alcohols, which is why amidation may proceed in the absence of catalysts by heating the reagents at 200–300 °C in the liquid phase. The removal of water with an excess of ammonia (or an amine) being used favours the attainment of a high degree of conversion. It is recommended to use acid catalysts, say P_2O_5 , in some cases.

It is known that carboxylic acid and an amine (or ammonia) form a salt, but the salt formed is not active upon amidation and its formation results in the deactivation of both reagents. Therefore, the salt has first to be dissociated into a free acid and an amine:



This is being followed by the amidation reaction, which proceeds by the following mechanism:



The rate of the reaction is proportional to the concentrations of free acid and amine (or ammonia), which are determined by the salt dissociation equilibrium. The equilibrium constant of this dissociation increases with increasing temperature, a fact which dictates the choice of the amidation temperature.

Like esterification, the amidation reaction can be accomplished under mild conditions by the action of acid chlorides:



Esters also react with ammonia and amines by a reversible reaction, the equilibrium of which is shifted to the right:



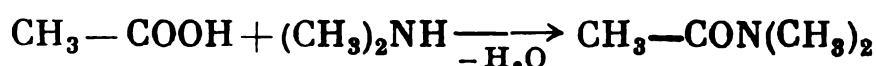
This reaction proceeds much more rapidly than the amidation of carboxylic acids themselves. It is effected without catalysts at 0–100 °C and is a convenient method of synthesis of some amides.

Amidation processes are of importance in the industry of basic organic and petrochemical synthesis for the production of a number of valuable compounds. The esters of formic acid, which are synthesized from carbon monoxide and alcohols in the presence of alkaline catalysts, are the starting materials for *dimethylformamide*:

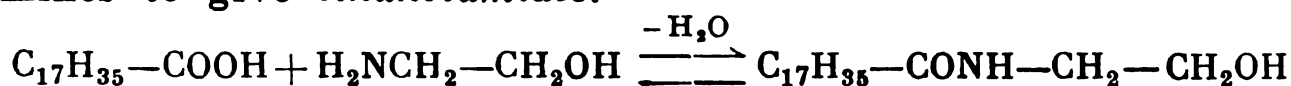


Dimethylformamide is a valuable solvent used for the absorption of acetylene from hydrocarbon gases, in the production of a polyacrylonitrile fibre, etc.

Acetic acid and dimethylamine are the starting materials for the solvent *dimethylacetamide*:

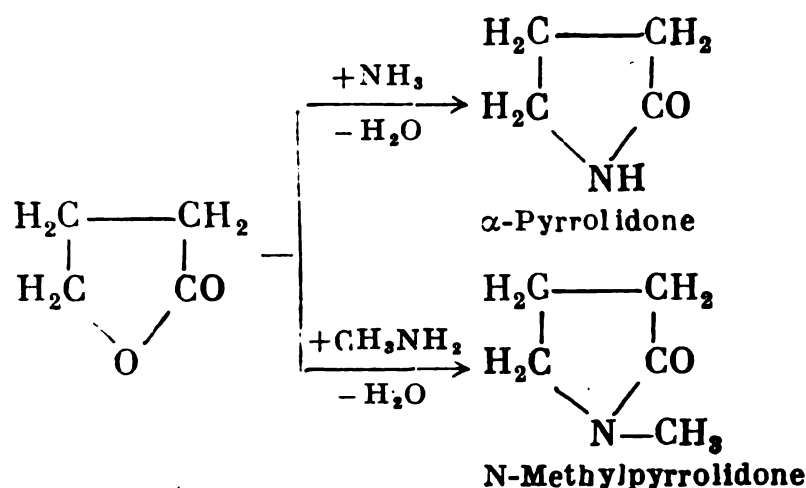


Stearic and other higher carboxylic acids react with ethanolamines to give *ethanolamides*:



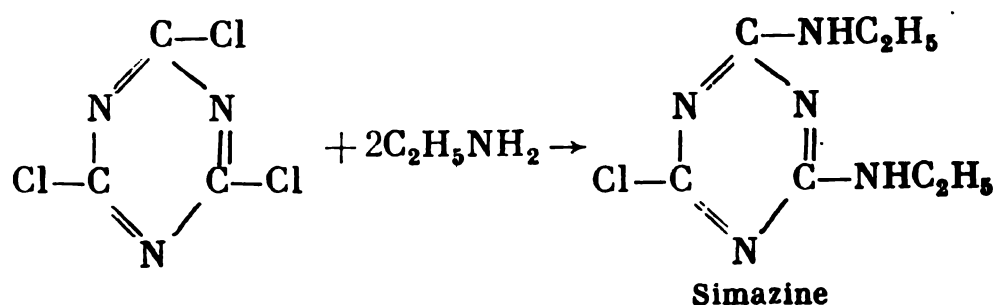
which possess good foam-forming properties and are used as components of detergents and for textile treatment.

The tendency to undergo amidation is also displayed by the inner esters of hydroxycarboxylic acids (lactones). γ -Butyrolactone and ammonia or methylamine are reacted to produce α -pyrrolidone and *N*-methylpyrrolidone:



α -Pyrrolidone is used for the production of a valuable monomer—*N*-vinylpyrrolidone and *N*-methylpyrrolidone is an excellent solvent and extractant (for example, for the isolation of acetylene from hydrocarbon gases).

The amidation reaction is the basic process for the synthesis of an important class of pesticides—partial amides of cyanuric acid. They are produced from cyanuric chloride and lower primary amines, say from ethylamine:



The propyl homologue of simazine is called propazine. Both compounds and also their analogues are effective herbicides.

There are several variants of the process for the production of nides from carboxylic acids or lactones.

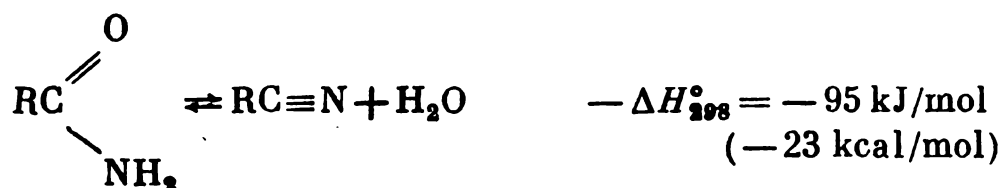
1. The reagents and the amide formed are slightly volatile (the production of ethanolamides of higher acids, etc). The process is carried out on heating up to 150-200 °C and the reaction is completed by the distillation of water (in vacuum, by blowing off with nitrogen).

2. The most volatile constituent of the reaction mass is one of the reagents (usually it is ammonia or an amine, just as in the production of lactams from lactones). The reaction is conducted at 200-300 °C in excess ammonia or amine under pressure, the pressure being required to maintain the reaction mass in the liquid state. With the acid and amide being slightly volatile the ammonia can be bubbled at atmospheric pressure; simultaneously, the ammonia purges the water formed, thereby contributing to the increase of the degree of conversion. The second variant is usually employed for the production of amides from esters, for which a temperature of 50-100 °C is required. For example, dimethylformamide can be produced at atmospheric or elevated pressure by bubbling gaseous methyl formate and dimethylamine through the reaction product with methanol being distilled off.

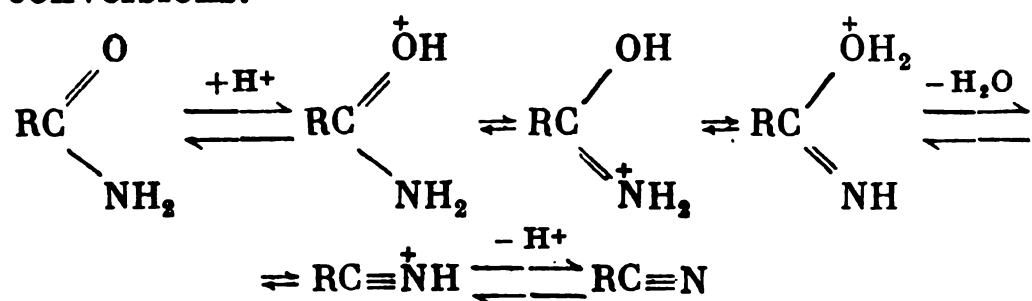
In some isolated cases, the synthesis of amides is carried out in the vapour phase. For instance, dimethylacetamide is obtained by passing the vapours of acetic acid and dimethylamine at about 50 °C through the reactor filled with aluminium oxide.

4.1.2. Dehydration of Amides and Hydration of Nitriles

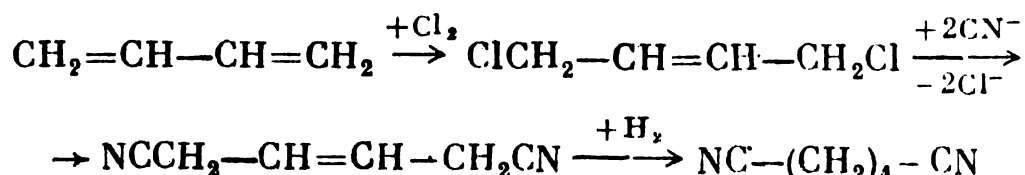
The dehydration of acid amides to nitriles is an equilibrium and strongly endothermic process:



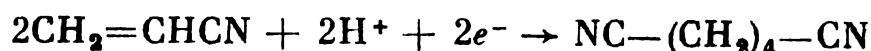
The equilibrium is shifted to the right only at 300–400 °C; for the reaction to be speeded up, acid-type catalysts are needed (phosphoric acid on a support, aluminium oxide, aluminosilicate, phosphates). The dehydration mechanism involves the following sequence of reversible conversions:



cyano groups:

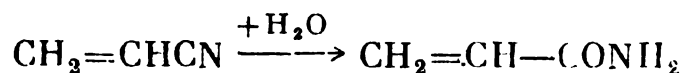


and the electrohydrodimerization of acrylonitrile:



All these methods have been realized on an industrial scale. Today, new methods are being developed, which are based on the catalytic addition of HCN to butadiene and the catalytic hydrodimerization of acrylonitrile, but in these cases a large amount of by-product isomeric dinitriles is formed.

In contrast to the dehydration of amides, the hydration of nitriles to acid amides is an exothermic reaction and at moderate temperatures it is practically irreversible. It is of primary interest for the synthesis of *acrylamide* from acrylonitrile:



Until recently this process was carried out using 80-85-percent sulphuric acid, which led to the consumption of an extra amount of the reagents and to the formation of ammonium sulphate wastes. It has recently been found that metallic copper is an effective catalyst for this process. The synthesis is carried out in an aqueous solution at 70-120 °C; the copper is filtered off from the reaction mass and the unchanged acrylonitrile is distilled out of it, both of them being then recycled to the reactor. The aqueous solution of acrylamide is evaporated to a concentration of 30-50 percent or until crystalline acrylamide is obtained.

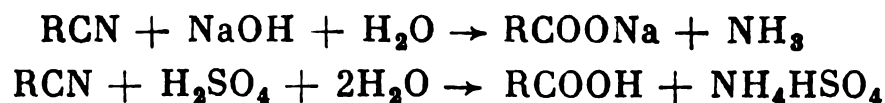
Acrylamide is readily polymerized to water-soluble polyacrylamide, which is a valuable flocculant extensively used for the separation of water suspensions, in flotation, in sewage and waste treatment, etc.

3.4.1.3. Hydrolysis and Esterification of Nitriles

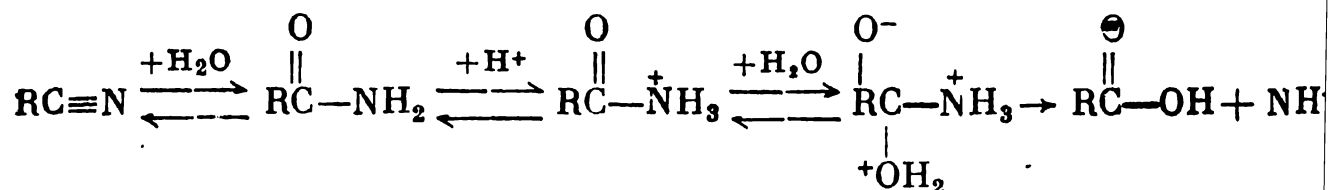
The hydrolysis of nitriles is one of the most extensively used methods of synthesis of carboxylic acids. This is due to the availability of many nitriles produced by the replacement of chlorine by a cyano group, by oxidative ammonolysis, cyanohydrination of carbonyl compounds, etc.

The hydrolysis of nitriles proceeds through the intermediate formation of amides and is catalyzed both by acids and alkalis. The catalysts bind the reaction products into salts, which makes the

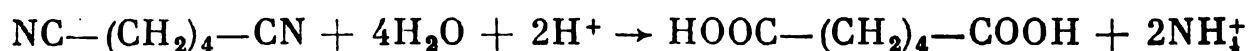
hydrolysis irreversible:



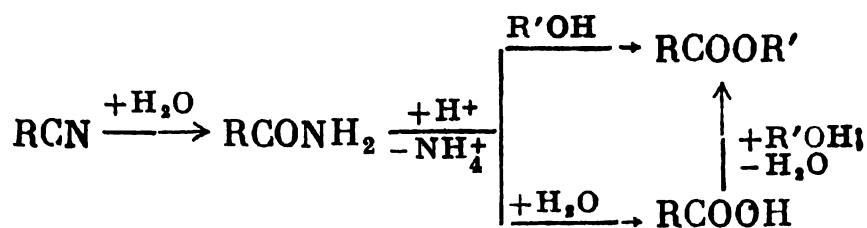
Usually, the acid hydrolysis, which yields a carboxylic acid in the free state, is more preferable. It is effected in an aqueous medium with the amount of acid not less than the stoichiometric amount at 50-80 °C and proceeds via the following steps:



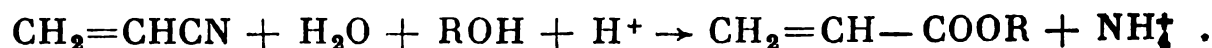
The reaction is strongly exothermic, which is why it is conducted with the nitrile being gradually poured into the heated solution of sulphuric acid in a stirred reactor being cooled. Phenylacetic acid, malonic acid, etc., are produced by this reaction. For example, if adipodinitrile is obtained from butadiene or acrylonitrile (pages 238-239), it can be hydrolyzed to give adipic acid:



If the end products are not the acids themselves but their esters, the hydrolysis of the nitrile may be combined with the esterification reaction. In such a case, the process is carried out with a mixture of water and alcohol, and sulphuric acid catalyzes both hydrolysis and esterification:

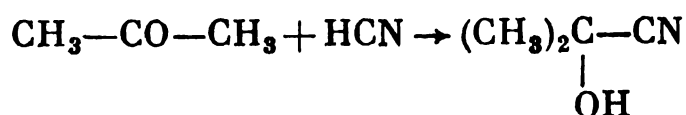


Until recently it was the most economical method of synthesis of esters of acrylic acid from acrylonitrile:

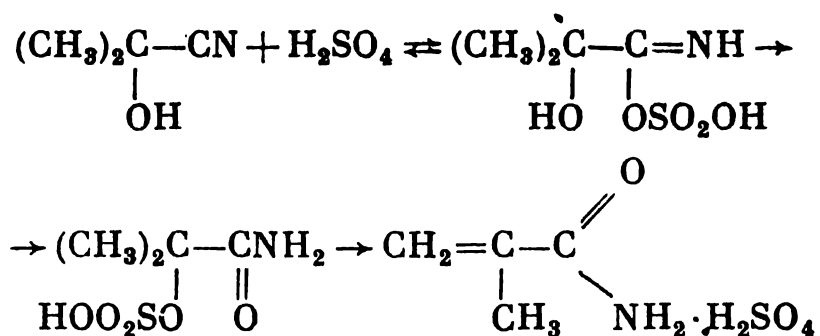


but today it is being replaced by a more efficient route of esterification of acrylic acid obtained by the oxidation of propylene (page 223).

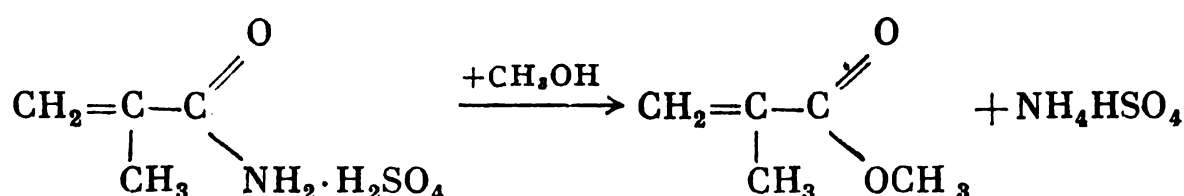
Acrylic acid and its esters were produced still earlier from acetaldehyde cyanohydrin. An analogous method is still of value and is present for the production of methacrylic acid and its esters. First *acetone cyanohydrin* is synthesized from acetone and hydrocyanic acid:



In an ordinary hydrolysis reaction, acetone cyanohydrin gives α -hydroxy-isobutyric acid, $(\text{CH}_3)_2\text{C}(\text{OH})\text{—COOH}$, but upon treatment with 100-percent sulphuric acid an imide is formed, which is dehydrated to give an unsaturated amide:



When water and methanol are added, esterification takes place; the catalyst used is sulphuric acid:



The by-products formed are dimethyl ether (due to the intermolecular dehydration of alcohol), the ester of α -hydroxyisobutyric acid, a small amount of resins and polymers.

A common shortcoming of the methods under consideration is the consumption of large quantities of sulphuric acid, which has to be used as a fertilizer of little value (ammonium sulphate). Also, a considerable amount of toxic waste waters is formed.†

Methyl methacrylate is still produced from acetone cyanohydrin by the route described above. The flow diagram of this process is given in Fig. 3.16. Acetone cyanohydrin (AC) and 100-percent sulphuric acid (monohydrate) in a molar ratio of 1 : 1.5 are continuously fed into mixer 1, where an imide is formed. The mixing operation liberates a large amount of heat, which is why the mixer is fitted with a stirrer and a coil for cooling, which can provide a temperature of 80–85 °C. The reaction mixture overflows through the side pipe into reactor 2, where a temperature of 130–135 °C is attained due to heating by steam. Under these conditions, the imide is converted to methacrylamide sulphate.

The resulting reaction mass is mixed with a certain amount of water and some of methanol and led to esterifying tray column 3 described earlier. This esterifying column is fitted with a boiler, with the aid of which the methyl methacrylate-water azeotrope and methanol are distilled out of the ammonium sulphate solution, which is then withdrawn from the still. Because of the high volatility part of the methanol is run to one of the lower trays of the

esterifying column in order to provide its presence on all the trays. The vapours of the azeotropic mixture and methanol are condensed in condenser-dephlegmator 4, part of the condensate being returned to esterifying column 3 as a reflux and the remainder withdrawn to refinery.

The first stage of the refining operation is the washing of the condensate by alkaline water in extraction column 5, where the methanol and acidic impurities (methacrylic acid) are washed off from the organic layer. Part of this aqueous extract may be used to dilute methacrylamide sulphate before it is led to esterifying column 3, the remainder being used in stripping column 6 to recover the

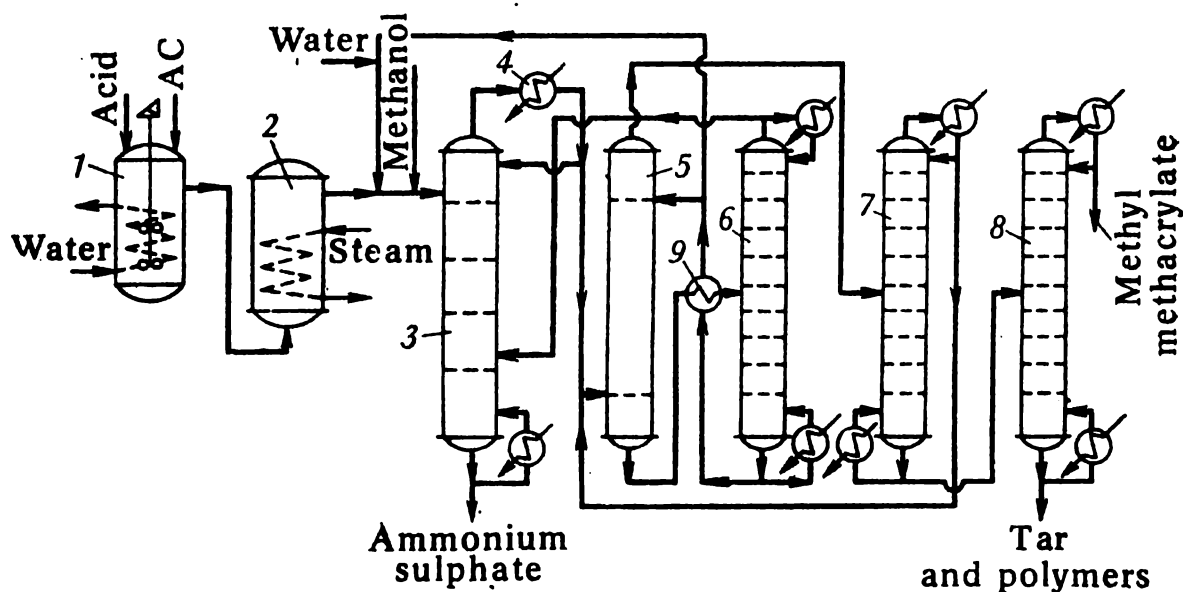


Fig. 3.16. Flow diagram of production of methyl methacrylate from acetone cyanohydrin:

1—mixer; 2—reactor; 3—esterifying column; 4—condenser-dephlegmator; 5—extraction column; 6—stripper; 7,8—fractionating columns; 9—heat exchanger.

methanol and the methyl methacrylate dissolved in the extract; they are then returned to the reaction. The organic layer from the top of extraction column 5 is run to fractionating column 7, where the azeotropic mixture of methyl methacrylate with water is distilled out and returned to extraction. The liquid from the still is transferred to column 8; the product taken overhead is pure methyl methacrylate; the tar and polymers are left in the still to be burned. In order to avoid the polymerization of methyl methacrylate, an inhibitor (hydroquinone) is added at the esterification and separation stages.

Because of the disadvantages of the sulphuric-acid hydrolysis of nitriles and cyanohydrins mentioned above, more economical methods of manufacture of methyl methacrylate are being developed. They are based on the oxidation of isobutylene and will be discussed in Chapter 6.

4.2. Synthesis and Conversions of Nitrogen Derivatives of Carbonic Acid

The synthesis of nitrogen derivatives of carbonic acid is an important application of amidation and esterification reactions for the synthesis of compounds genetically related to carbonic acid—its amides, amidoesters, and also derivatives of isocyanic acid ($\text{N}=\text{C}=\text{O}$) and cyanic acid ($\text{HO}-\text{C}\equiv\text{N}$).

4.2.1. Synthesis of Isocyanates

Isocyanates, $\text{RN}=\text{C}=\text{O}$, have assumed great industrial significance in recent years for the production of polymeric materials (polyurethanes) and pesticides belonging to the class of esters of carbamic acid (carbamates).

Isocyanates are synthesized from phosgene and primary amines (by the amidation of phosgene or the phosgenation of an amine). As is well known, the interaction of these compounds in the presence of an excess of an amine leads to substituted carbamides. In order to avoid their formation and to produce isocyanates, the process is conducted with equimolar ratios of phosgene to amine or even with an excess of phosgene in a solution of toluene, chlorobenzene or *o*-dichlorobenzene.

The first stage consists of the interaction of phosgene with an amine leading to the formation of carbamoyl chloride (the acid chloride of alkylcarbamic acid) and amine hydrochloride:



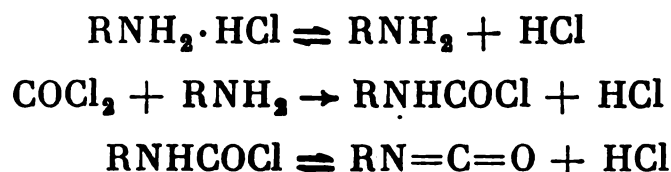
In order to prevent the formation of carbamides



The amine is added to the phosgene dissolved in one of the solvents listed above so that phosgene is in excess with respect to the amine. For example, half of the required phosgene is dissolved in chlorobenzene and all of the amine is added in the cold (0°C) on stirring. This gives a solution of carbamoyl chloride and a suspension of amine hydrochloride in the solvent. The carbamoyl chloride reacts with the amine only to a small extent, since it is much less reactive than phosgene (compare with the stepwise esterification of phosgene with alcohols; page 231).

In the second stage, the suspension obtained is heated up to $50\text{--}200^\circ\text{C}$ and the remaining amount of phosgene in some excess, which is required for the amine hydrochloride to be dissolved completely, is passed through the heated suspension. At elevated temperature the amine hydrochloride dissociates, the phosgene reacts with the liberated amine, and the carbamoyl chloride splits off HCl ,

giving an isocyanate:



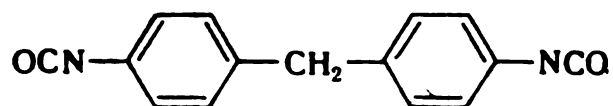
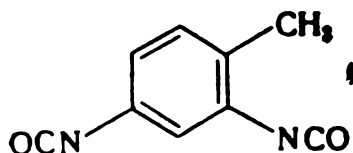
The overall reaction is as follows:



In the batch operation, the synthesis is carried out in a stirred reactor fitted with a bubbler for phosgene, a jacket and coils for cooling and heating and also with a reflux condenser. Upon completion of the reaction the solution is purged with nitrogen in order to separate the traces of phosgene and hydrogen chloride and is subjected to distillation to isolate the commercial isocyanate; the solvent is then regenerated. The excess phosgene carried over from the reactor by the HCl gas is absorbed by the solvent that was used for the reaction, the resulting solution being then utilized for subsequent operations.

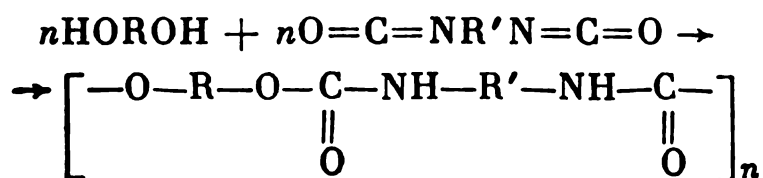
There has also been developed a continuous process of liquid phase synthesis of isocyanates under pressure required for keeping the phosgene in the dissolved state. In one of the methods, the process is carried out in two steps in two separate reactors; one operates at a low temperature and the other at a higher temperature (150-200 °C), i.e., the continuous variant of the batch process described above is realized. In another method, the reaction is conducted in one step in a column-type reactor at a high temperature (about 200 °C). The excess phosgene is extracted from the effluent gas (HCl) by the solvent and is recycled to the reaction. The yield of isocyanates exceeds 90 percent.

Of greatest importance among the isocyanates are *m*-toluylene diisocyanate (produced from *m*-tolylenediamine) and diphenylmethane diisocyanate (produced from 4,4-diaminodiphenylmethane and its oligomers, which are synthesized from aniline and formaldehyde by an acid-catalyzed reaction):



Diisocyanates are used to manufacture valuable high-molecular-weight compounds—polyurethanes (the products of the copolymerization with glycols—1,4-butanediol, ethylene and propylene glycols) and polyester urethanes (the products of the polymerization with low-molecular-weight polyesters containing hydroxyl groups at the ends and produced from adipic and other dicarboxylic acids

excess glycol):



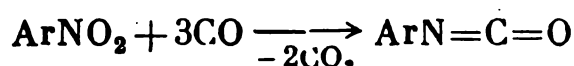
polyurethanes and polyester urethanes are used for the manufacture of synthetic fibres, rubbers, lacquers and glues. They are also used in the production of foamed plastics (Porolon), for which purpose a small amount of water is added during the polymerization process; the added water hydrolyzes part of isocyanate groups to give off carbon dioxide:



The function of carbon dioxide is to foam the polymer, which thus assumes a porous structure.

The industry also produces a number of monoisocyanates (phenyl, chlorophenyl and methyl isocyanates) used in the synthesis of carbamates and substituted carbamides.

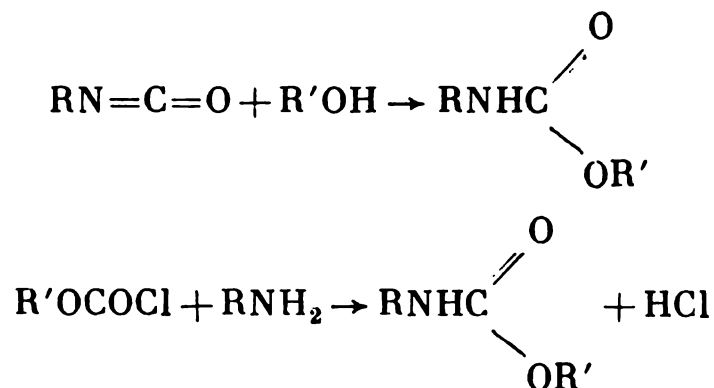
Another, more economical method of producing isocyanates has recently been developed, which consists of the catalytic carbonylation of nitro compounds:



In this method, amines and phosgene are not synthesized, expensive chlorine is not used, etc.

3.2.2. Synthesis of Carbamates (Urethanes)

The esters of alkyl- and arylcarbamic acids (*carbamates* or *urethanes*), $\text{RNHCOOR}'$, are produced by two principal methods—the reaction of isocyanates with alcohols or the amidation of the esters of chlorocarbonic acid:



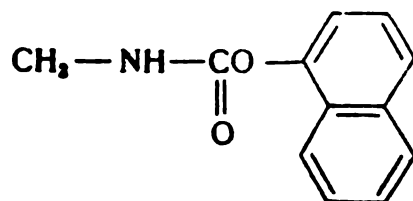
Both reactions are exothermic and practically irreversible. The carbonylation of isocyanates is carried out at 60–80 °C and the isocyanate is gradually added upon stirring to an excess of alcohol. Solvents (carbon tetrachloride, etc.) may be used for the reaction with crystalline phenols. The amidation of chlorocarbonic esters is anal-

ogous to the above-described synthesis of esters or amides from the acid chlorides of acids. Both methods give a high yield of an urethane (more than 95 percent) and have similar economical indices.

Many of the esters of substituted carbamic acids are valuable pesticides, which decompose rather readily under natural conditions with the formation of slightly toxic compounds. They include the well-known herbicides—the isopropyl esters of N-phenylcarbamic and 3-chloro-N-phenylcarbamic acid:

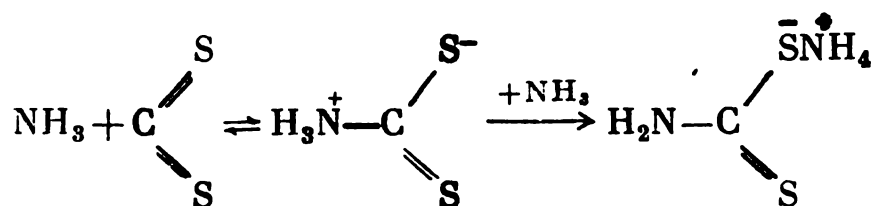


and a very effective insecticide—the α -naphthyl ester of methylcarbamic acid (Sevin or Arylam):

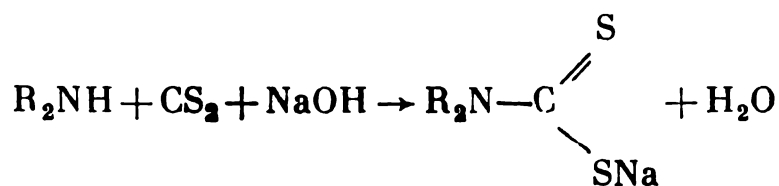


which can be produced from methyl isocyanate and α -naphthol or from the α -naphthyl ester of chlorocarbonic acid and methylamine.

Dithiocarbamates (dithiourethanes). Unlike carbamates, the salts of alkyl dithiocarbamic acids (*dithiocarbamates*) are easily obtained by the direct amidation of carbon disulphide by ammonia or amines:

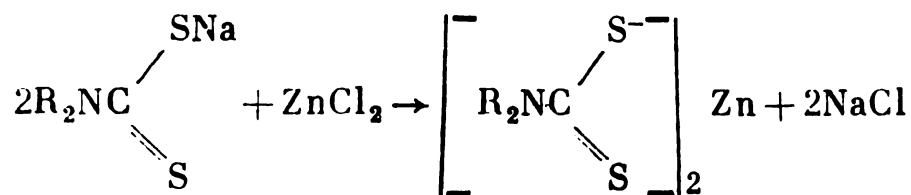


The reaction is usually effected with an equimolar ratio of the reagents in the presence of sodium hydroxide:

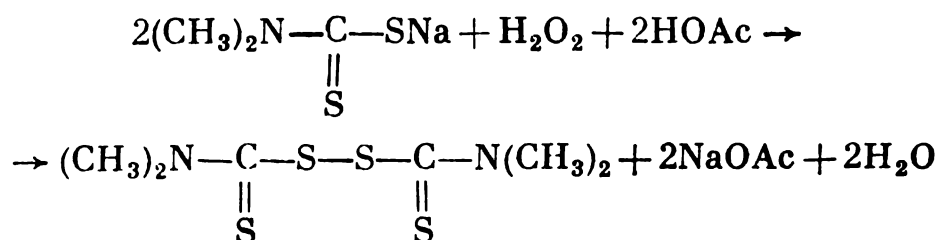


The process is carried out in an aqueous medium by gradually adding carbon disulphide (in an excess of 3-4 percent based on the amine) to the well stirred aqueous solution of the amine and sodium hydroxide (the excess of sodium hydroxide is about 5 percent with respect to the amine) at 25-35 °C. When the reaction is complete, the liquid is neutralized and the dithiocarbamate is derived as

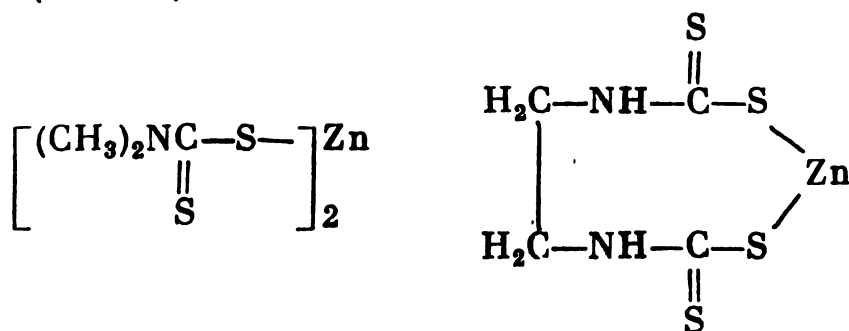
insoluble salts of zinc, manganese, etc.:



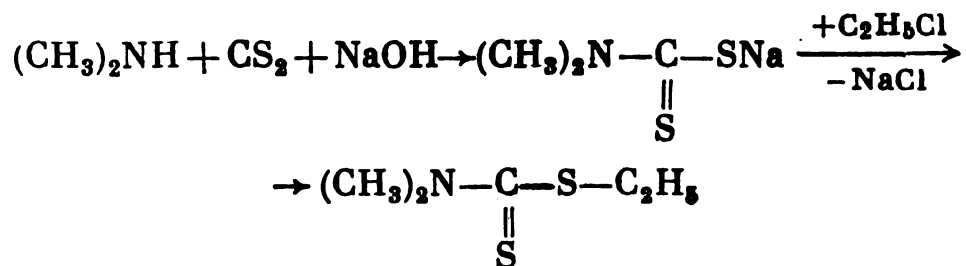
Zinc diethyldithiocarbamate is used as a rubber vulcanization accelerator. Use is made for the same purpose of bis(dimethylthiocarbamoyl)disulphide, which is known as *tetramethylthiuram disulphide* or *thiram*. It is made by the oxidation of a solution of sodium dimethyldithiocarbamate by hydrogen peroxide or chlorine:



Tetramethylthiuram disulphide (*thiram*) and certain salts of dithiocarbamic acid are also valuable pesticides. Of these, mention should be made of *zinc dimethyldithiocarbamate* (*ziram*) and also of *zinc ethylenebisdithiocarbamate* (*zineb*) and *manganese ethylenebisdithiocarbamate* (*maneb*):



The esters of dithiocarbamic acid (*dithiourethanes*) also find application as pesticides. They are produced from the salts of dithiocarbamic acid by treatment with alkyl chlorides upon heating under pressure:



3.4.2.3. Substituted Carbamides

These compounds are also widely used as pesticides. The most important of these compounds are N-aryl-N',N'-dialkylcarbamides, which possess high herbicide activity. The general method for their

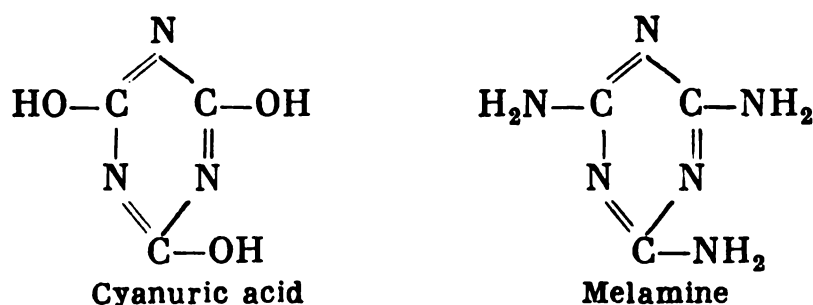
production is the interaction of an aryl isocyanate with dialkylamines; an example is the reaction of phenyl isocyanate with dimethylamine in the synthesis of phenacetamide (*Phenurone*):



The 3,4-dichlorophenyl analogue of Phenurone, which is known as *diuron*, is even more active.

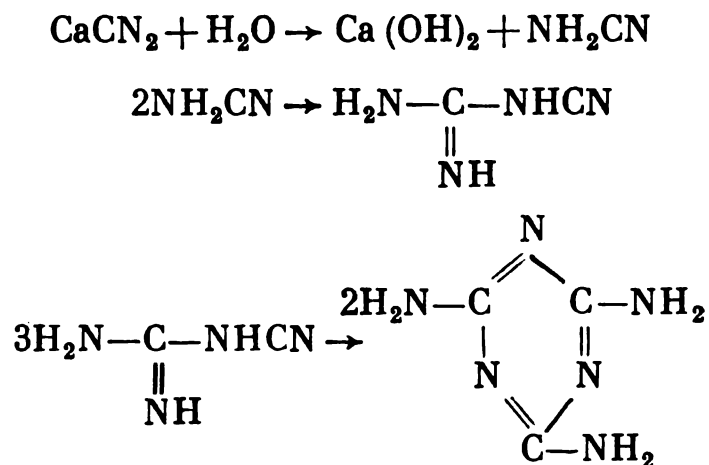
3.4.2.4. Synthesis of Melamine

Melamine, which is the amide of cyanuric acid,



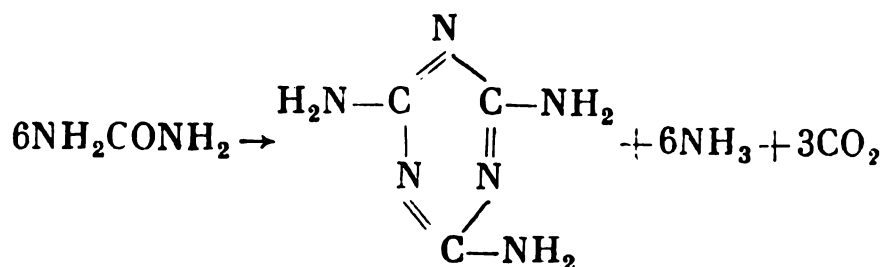
is a colourless crystalline compound (m.p. 354 °C). It is moderately soluble in water, lower alcohols, liquid ammonia. Melamine is most important as one of the components in the synthesis of melamine-formaldehyde polymers, which are noted for high thermal stability and mechanical strength and which are of great value for the production of plastics.

Melamine has been produced for a long period of time by a single method of industrial synthesis based on calcium cyanamide, CaCN_2 . The free cyanamide, NH_2CH , whose trimer is melamine, is but slightly stable. Therefore, melamine is obtained through the dicyandiamide step; dicyandiamide is formed upon boiling of calcium cyanamide with water at $\text{pH} = 9$:

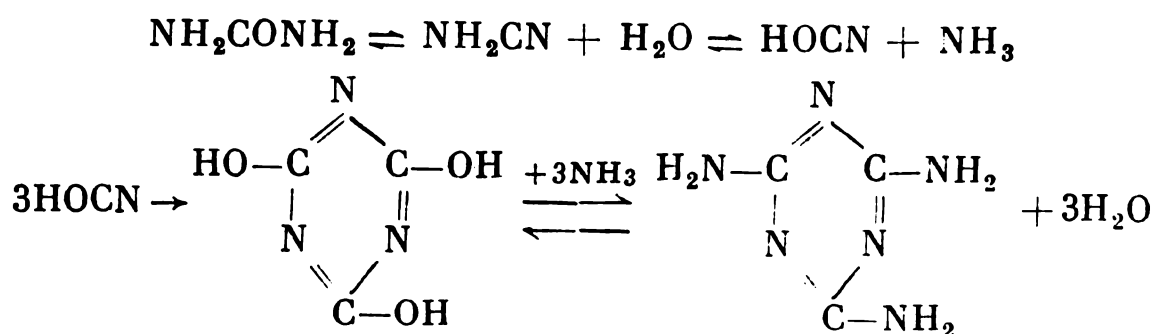


The energy consumption and capital cost of the production of calcium carbide and cyanamide have led to searches for other routes to melamine.

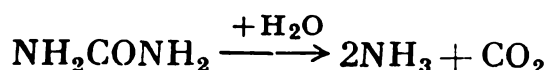
The most important route is based on carbamide. The reaction described by the following overall equation:



The mechanism of the reaction is very complicated and involves the dehydration of carbamide to cyanamide and the hydrolysis of cyanamide to cyanic acid under the influence of the liberated water. The cyanic acid is then trimerized to cyanuric acid, which undergoes amidation by ammonia to give melamine:



The liberated water decomposes carbamide (or the intermediates) at a high temperature to yield ammonia and carbon dioxide:



which accounts for their presence in the above overall reaction equation. When the ammonia and carbon dioxide are returned to the synthesis of carbamide, there is realized a closed melamine production cycle. It has been observed that the addition of ammonia to the starting carbamide prevents the formation of by-product higher condensation products and improves the yield of melamine. Therefore the mixture supplied to the reaction contains up to 0.75 mole of NH_3 per mole of $\text{CO}(\text{NH}_2)_2$.

The process has been realized industrially in two variants. In the first variant, the process is operated batchwise at 400-500 °C and 8-10 MPa. The continuous process is more efficient: a pressure close to atmospheric is used and the process is conducted in two steps—the formation of cyanic acid and the formation of melamine. The first step requires a heterogeneous acid-type catalyst and is strongly endothermic. To maintain the required temperature (320-330 °C), use is made of reactors heated by fuel gases. The second step is exothermic and is carried out in an adiabatic reactor; the gas-vapour mixture being heated up to 460 °C due to the heat of reaction.

The flow diagram of melamine production from carbamide by the continuous process is given in Fig. 3.17.

The carbamide from hopper 1 is run by conveyer 2 to reactor 3 heated by flue gases. The reactor may be a column with a fluidized catalyst bed. The mixture formed in the reactor passes together with ammonia directly into the second reaction unit 4, where the synthesis of melamine takes place. The mixture consisting of ammonia, carbon dioxide and sublimed melamine is cooled in mixer 5 due to the injection of cold water. In separator 6 the carbon dioxide, ammonia and the water vapours are separated from the melamine

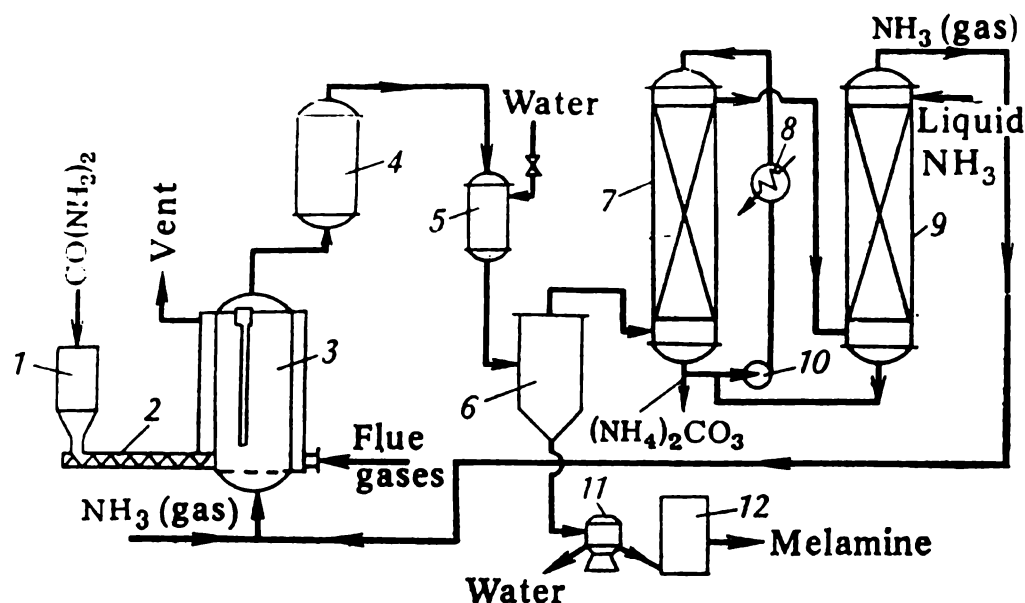


Fig. 3.17. Flow diagram of melamine production from carbamide:

1—hopper; 2—transfer conveyer; 3,4—reactors; 5—mixer; 6—separator; 7—scrubber; 8—cooler; 9—drying column; 10—pump; 11—centrifuge; 12—drier.

suspension in water. The gas-vapour mixture is then led to a packed scrubber 7 refluxed by the aqueous solution of ammonia which has been chilled in cooler 8. The water is condensed and the carbon dioxide and ammonia give ammonium carbonate, an aqueous solution of which is withdrawn from the still of column 7 and sent to the carbamide production plant. The excess ammonia that has not been absorbed in scrubber 7 is freed from the water in packed column 9, which is refluxed by liquid ammonia (the evaporation of liquid ammonia favours the condensation of water). The ammonia water is led from the still of column 9 to unit 7, where it is utilized for the absorption of carbon dioxide, and the recirculating ammonia gas is returned to reactor 3.

The suspension of melamine in water passes from separator 6 to centrifuge 11, where the major proportion of water is separated. The wet melamine is then dried and pulverized, after which the commercial product is sent to the consumer. The yield of melamine is 85-95 percent.

ALKYLATION PROCESSES

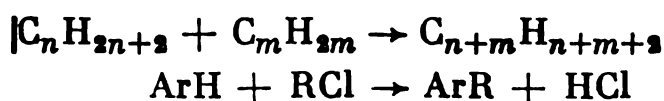
Alkylation is the term used for processes in which alkyl groups are introduced into molecules of organic and some inorganic compounds. These reactions are of great practical value for the synthesis of nuclear-alkylated aromatic compounds, isoparaffins, many mercaptans and sulphides, amines, compounds having an ether bond, organoelement and organometallic compounds, and products obtained by processing α -oxides and acetylene. Alkylation reactions are often intermediate steps in the production of monomers, detergents, etc.

Many alkylation products are manufactured industrially on a large scale. For example, in the USA the forecast for 1980 was more than 30,000,000 tons of isoparaffinic alkylate, 4,000,000 tons of ethylbenzene, 1,500,000 tons of isopropylbenzene, 400,000 tons of higher alkylbenzenes, about 4,000,000 tons of glycols and other conversion products of α -oxides, etc.

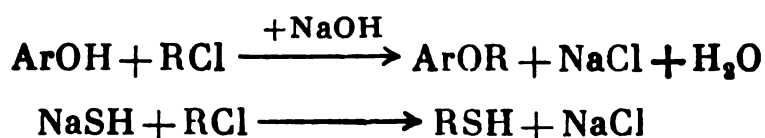
4.1. General Description of Alkylation Reactions

Classification of Alkylation Reactions. The most rational classification of alkylation processes is based on the type of the bond formed.

Alkylation at the carbon atom (C-alkylation) consists of the substitution of an alkyl group for the hydrogen atom attached to a carbon atom. The tendency to undergo this substitution is displayed by paraffinic hydrocarbons, but aromatic compounds are most liable to undergo the alkylation reaction (the Friedel-Crafts reaction):



Alkylation at oxygen and sulphur atoms (O- and S-alkylations) is a reaction, as a result of which the alkyl group becomes attached to an oxygen (or sulphur) atom:



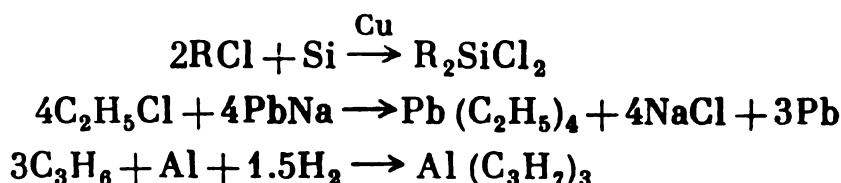
It is easy to see that in this particular case the general definition of alkylation includes also processes, such as the hydrolysis of chloro derivatives or the hydration of olefins, from which it follows that the term alkylation should be applied only to reactions which involve the introduction of the alkyl group and which do not belong to other classifications.

Alkylation at the nitrogen atom (N-alkylation) consists of the replacement of hydrogen atoms in ammonia or in amines by alkyl groups. This is the most important method of synthesis of amines:



N-Alkylation is sometimes classified as the *ammonolysis* (or *aminolysis*) of organic compounds.

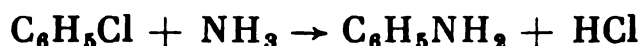
Alkylation at atoms of other elements (Si-, Pb- and Al-alkylations) is the most important method of producing organoelement and organometallic compounds, in which the alkyl group becomes directly attached to a heteroatom:



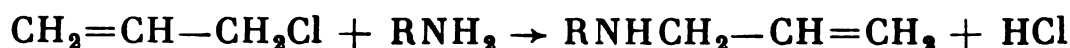
Another classification of alkylation reactions is based on the differences in the structure of the alkyl group to be introduced into an organic or inorganic compound. It may be a saturated aliphatic group (say, an ethyl or an isopropyl group) or a cyclic group. In the latter case, the reaction is sometimes called *cycloalkylation*:



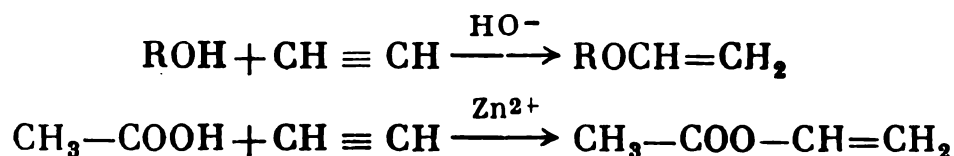
When a phenyl group or generally an aryl group is introduced, a direct bond is formed with a carbon atom of the aromatic ring (*arylation*):



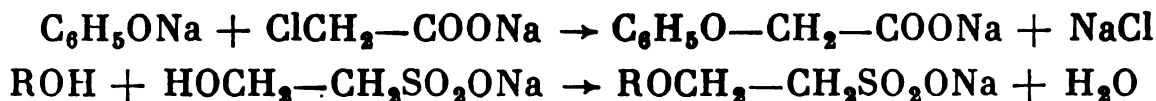
The alkyl group may contain an aromatic ring or a double bond and if these are sufficiently remote from the reaction centre, the reaction differs little from ordinary alkylation processes:



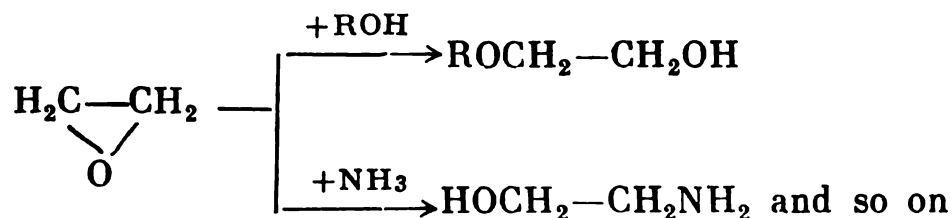
However, the introduction of the vinyl group (*vinylation*) holds a special position and is effected using mainly acetylene:



Finally, the alkyl groups may contain various substituents, say chlorine atoms, and hydroxyl, carboxyl, and sulpho groups, etc.:



The most important of the reactions, in which substituted alkyl groups are introduced, is *β-oxyalkylation* (in a particular case, *oxyethylation*), which embraces a wide range of reactions of olefin oxides:

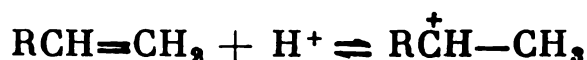


Alkylating Agents and Catalysts. According to the nature of the bond to be broken upon alkylation, all alkylating agents should be classified into the following groups:

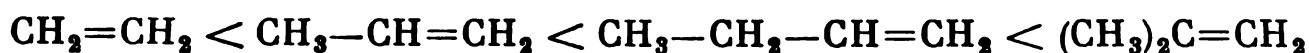
- (1) unsaturated compounds (olefins and acetylene), in which the π -electron bond between carbon atoms is broken;
- (2) chloro derivatives having a sufficiently mobile chlorine atom, which is capable of being replaced under the action of various agents;
- (3) alcohols, ethers and esters, in particular olefin oxides, in which the carbon-oxygen bond is ruptured.

Olefins (ethylene, propylene, butylenes and higher olefins) are of prime importance as alkylating agents. Because of their low cost, the tendency is to use them as often as possible. They are used mainly for the C-alkylation of paraffin hydrocarbons and aromatic compounds. Olefins are much less effective as alkylating agents in O- and N-alkylations and also in the synthesis of numerous organometallic compounds.

The alkylation by olefins often proceeds by an ionic mechanism via the intermediate formation of carbonium ions and is catalyzed by protic and aprotic acids. The reactivity of olefins in such reactions depends on their ability to form carbonium ions:



This means that the ability of olefins to effect alkylation considerably increases with increasing length and degree of branching of the carbon chain:

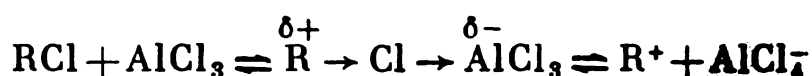


Sometimes the alkylation by olefins proceeds under the action of initiators of radical-chain reactions, light or high temperature. Here, the intermediate active particles are free radicals. The reactivities of olefins in such reactions become closer.

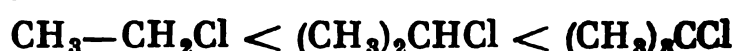
Chloro derivatives are alkylating agents, whose scope of applica-

tion is the widest. They are suitable for C-, O-, S- and N-alkylations and for the synthesis of most organoelement and organometallic compounds. The use of chloro derivatives is rational for those processes where they cannot be replaced by olefins or where chloro derivatives are cheaper and more available than olefins.

The alkylating action of chloro derivatives is manifested in three different types of interaction: electrophilic reactions, nucleophilic substitutions and free-radical processes. The mechanism of electrophilic substitution is mainly characteristic of the alkylation at the carbon atom, but, in contrast to olefins, the reactions are catalyzed only by aprotic acids (aluminium and iron chlorides, etc.). In the limiting case, the process occurs with the intermediate formation of a carbonium ion:



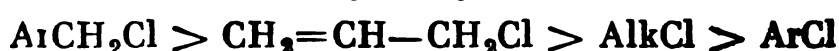
which is why the reactivity of alkyl chlorides depends on the polarization of the C—Cl bond or on the stability of carbonium ions and increases with increasing length and degree of branching of the alkyl group:



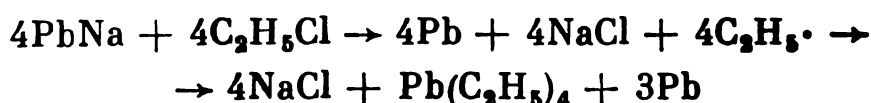
In a different type of reactions characteristic of alkylations at oxygen, sulphur, and nitrogen atoms, the process consists of the nucleophilic substitution of a chlorine atom. The mechanism is analogous to the hydrolysis of chloro derivatives; the reaction proceeds, as a rule, in the absence of catalysts:



The reactivity of chloro derivatives increases in such processes in the same order as with hydrolysis reactions, namely:

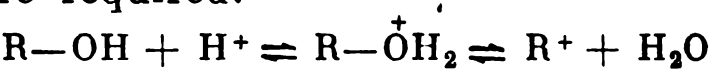


Quite a number of alkylation processes effected by chloro derivatives occurs by a free-radical mechanism. This is especially characteristic of the synthesis of organoelement and organometallic compounds, when free radicals are generated as a result of the interaction with metals:



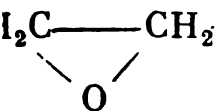
Alcohols and ethers are capable of effecting C-, O-, N- and S-alkylation reactions. The ethers may also include olefin oxides, which are the inner ethers of glycols; of all ethers, only olefin oxides are used in practice as alkylating agents. Alcohols are used for O- and N-alkylations if they are cheaper and more readily available than

chloro derivatives. In order to rupture their alkyl-oxygen bond, acid catalysts are required:



Energy Characteristics of Principal Alkylation Reactions. Depending on the alkylating agent and the type of the bond to be broken in the compound to be alkylated, alkylation processes strongly differ by their energy characteristics. The heat effects for the gaseous state of all compounds in some important C-, O- and N-alkylations are given in Table 4.1. Since they depend significantly on the structure of the compound to be alkylated, Table 4.1 gives the most frequently encountered ranges of variation of the heat effects.

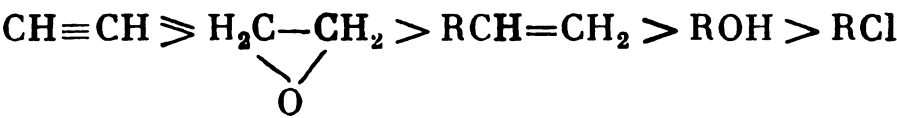
TABLE 4.1. The Heat Effects of the Most Important Alkylation Reactions

Alkylating agent	Bond being broken	Heat of reaction	
		kJ/mol	kcal/mol
CH=CH ₂	C _{aliph} -H	84-100	20-24
	C _{arom} -H	96-104	23-25
	O-H	50-63	12-15
Cl	C _{arom} -H	34-42	8-10
	O-H	≈ 0	≈ 0
	N-H	0-25	0-6
OH	O-H	0-21	0-5
	N-H	21-42	5-10
	O-H	88-104	21-25
H≡CH	O-H	100-117	24-28

A comparison of the data presented in Table 4.1 shows that when the same alkylating agent is used, the heat of reaction in alkylations at different atoms decreases in the following order:



and for different alkylating agents it varies as follows:



The especially high heat effect of alkylation involving ethylene oxide and acetylene is due to the considerable strain of the three-membered oxide ring and the high endothermicity of compounds having a triple bond.

Some of the reactions presented in Table 4.1 are reversible; the conditions for their equilibrium will be considered in sections concerned with the physico-chemical regularities of particular processes.

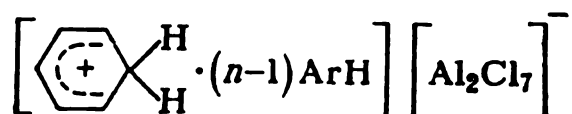
4.2. C-Alkylation

These processes include very important (industrially) alkylation reactions of aromatic compounds in the nucleus and the alkylation of paraffinic hydrocarbons. In general outline they may be subdivided into alkylations at an aromatic carbon atom and alkylations at a saturated carbon atom.

4.2.1. Chemistry and Theory of the Alkylation of Aromatic Compounds in the Ring

Catalysts. When aromatic hydrocarbons (benzene, toluene, etc.) are to be alkylated by chloro derivatives, the only catalyst used is aluminium chloride, which is the most active of all currently available aprotic catalysts. It is also used for the alkylation of hydrocarbons by olefins, but in this case other acid catalysts are also suitable (H_2SO_4 , anhydrous HF, BF_3 , supported phosphoric acid, aluminosilicates, zeolites). The process is carried out in the liquid phase at 10-40 °C and 0.1-1 MPa in the presence of H_2SO_4 and HF, in the vapour phase at 225-275 °C and 2-6 MPa with H_3PO_4 as catalyst, in the liquid or vapour phase at 200-400 °C and the same pressure with aluminosilicates and zeolites. A solid phosphoric-acid catalyst was at one time widely employed for alkylation reactions, but today zeolites are of greater value; aluminium chloride, which has a number of advantages over other catalysts, is of prime industrial significance.

Aluminium chloride in the solid state is practically insoluble in hydrocarbons and does not strongly catalyze the reaction. However, as HCl is liberated aluminium chloride begins to be converted into a dark liquid substance which is also insoluble in excess hydrocarbon. This Gustavson complex possesses high catalytic activity and the reaction is gradually speeded up. It can be prepared by passing HCl on heating through a suspension of AlCl_3 in an aromatic hydrocarbon. The complex is a compound consisting of AlCl_3 and HCl with 1-6 molecules of an aromatic hydrocarbon, one of which is in a special structural state of a positively charged ion (a δ -complex), the remaining atoms forming the solvation shell:



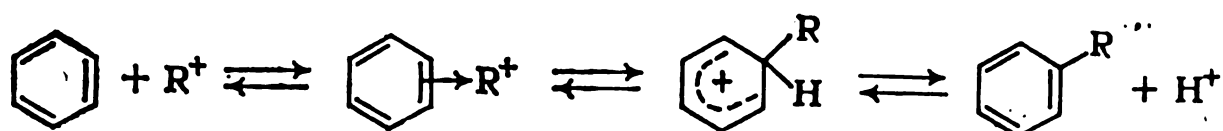
In order to prevent the slow catalysis by solid aluminium chloride, it is expedient to prepare this active catalytic complex preliminarily and then to introduce it into the reaction. Apart from HCl, its formation is favoured by small amounts of water or an appropriate chloro derivative, whose function is to generate HCl. The use of HCl or RCl is more suitable since water deactivates part of the catalyst by decomposing it. For the same reason, it is necessary to dry the reagents well and to see that measures are taken to prevent the entry of water into the reaction mixture because water can cause a vigorous decomposition of the complex. Other catalyst poisons are many sulphur compounds and ammonia and, to a lesser degree, dienes and acetylene. Thus, the liquid reaction mass upon alkylation in the presence of aluminium chloride consists of two phases: the catalytic complex and the hydrocarbon layer.

Reaction Mechanism. The most important alkylating agents used on an industrial scale are chloro derivatives and olefins. The use of alcohols is less effective because upon alcoholic alkylation aluminium chloride is decomposed and proton acids are diluted with the water formed. In both cases, the catalyst is deactivated, which is why large quantities of the catalyst are needed.

In reactions effected by chloro derivatives and olefins aluminium chloride is consumed only in catalytic amounts. With chloro derivatives aluminium chloride activates the chlorine atom, forming a strongly polarized complex or a carbonium ion (page 254); with olefins this occurs only in the presence of a cocatalyst—hydrogen chloride:

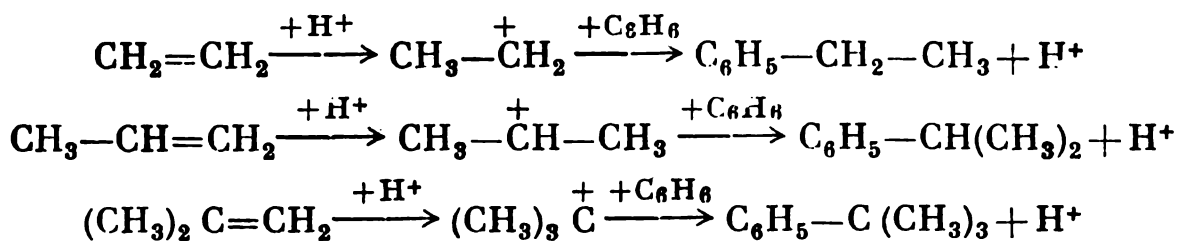


Indeed, upon catalysis by an aluminium chloride-hydrocarbon complex the proton required is already present in the form of a δ -complex. It is transferred to the olefin molecule and the carbonium ion formed attacks the aromatic compound, the entire reaction taking place in the layer of the catalytic complex, which continuously exchanges its ligands with the hydrocarbon layer. The carbonium ion (or the strongly polarized complex) formed in one or other way attacks then the aromatic ring and the reaction proceeds through the intermediate formation of a π -complex and a carbonium ion and is followed by the fast proton elimination step:

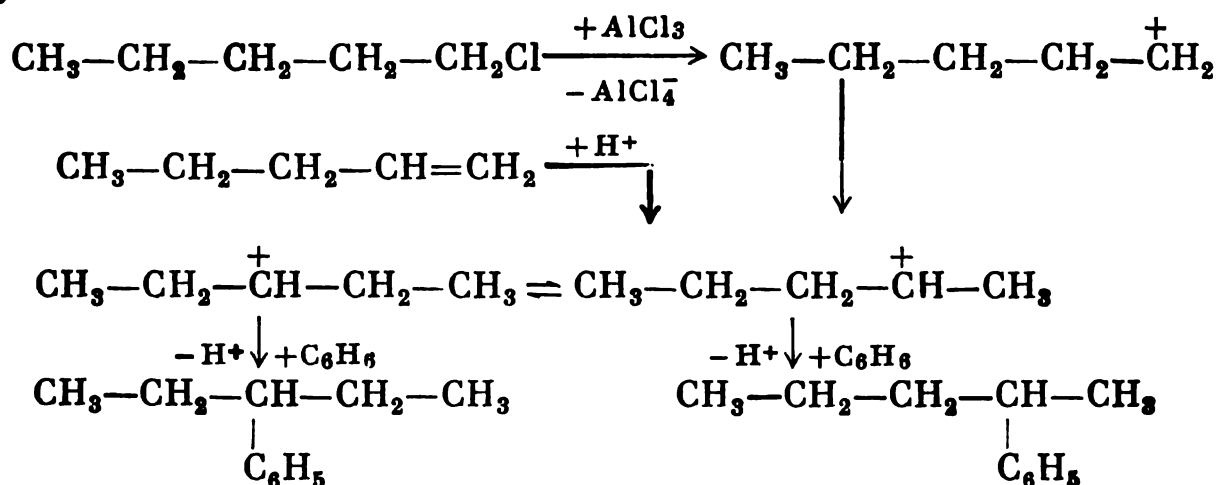


The structure of the alkyl group in the resulting product is determined by the rule of the intermediate formation of the most stable carbonium ion (*tert*- > *sec*- > *prim*-). Therefore, with lower olefins

ethylene gives only a primary alkylbenzene (ethylbenzene), propylene forms only a secondary alkylbenzene (isopropylbenzene) and isobutylene yields only *tert*-butylbenzene:

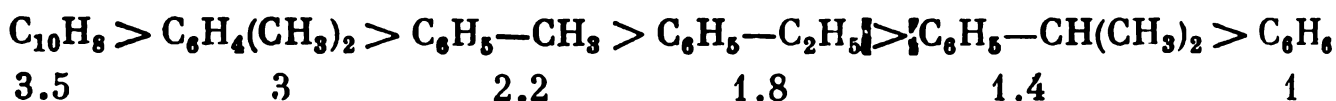


However, upon alkylation by higher olefins and chloro derivatives the alkyl groups undergo isomerization, which precedes the alkylation, since alkylbenzenes are not capable of undergoing isomerization. This isomerization proceeds in the direction of the intermediate formation of a most stable carbonium ion but the hydrocarbon skeleton of the alkyl group remains intact and only the reaction centre is displaced. As a result of this, chloro derivatives and olefins with a straight chain of carbon atoms give a mixture of secondary alkylbenzenes:



and compounds with a branched carbon chain give predominantly *tert*-alkylbenzenes.

The effect of the structure of an aromatic compound in alkylation reactions is generally the same as in other electrophilic substitutions in the aromatic nucleus, but alkylation reactions have its own specific features. Alkylation reactions are relatively weakly sensitive to electron-donating substituents in the ring. For example, the activating effect of alkyl groups and condensed rings upon catalysis in the presence of aluminium chloride increases in the following sequence (for benzene the value is taken to be equal to unity):

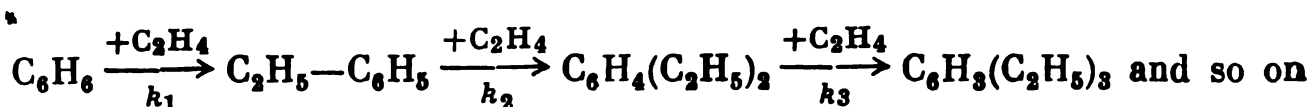


Electron-attracting substituents deactivate strongly the aromatic ring. Chlorobenzene is alkylated 10 times more slowly than ben-

zene, and carbonyl, carboxyl, cyano and nitro groups deactivate the aromatic ring completely, as a result of which the corresponding derivatives are not capable of alkylation. In this respect, the alkylation reaction differs significantly from other substitutions in the aromatic ring, say from chlorination and sulphonation.

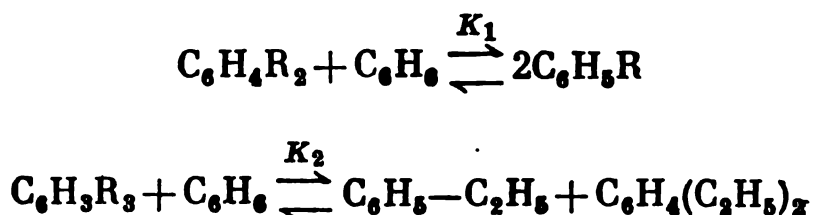
The orientation rules for alkylations are in general similar to those for other electrophilic substitutions in the aromatic ring, but the structure of the product may vary substantially, depending on the catalyst used and the reaction conditions. For instance, electron-donating substituents and halogen atoms direct further substitution predominantly to *para*- and *ortho*-positions, but under more severe conditions and especially upon catalysis in the presence of aluminium chloride there takes place the isomerization of benzene homologues which involves an intramolecular migration of alkyl groups and the formation of equilibrium mixtures, in which the thermodynamically most stable isomers predominate. This reaction has already been discussed in connection with the isomerization of xylenes to more valuable isomers (page 77), but it also occurs with other alkyl groups. In the alkylation of naphthalene, this makes it possible to obtain 1-alkylnaphthalene under mild conditions and 2-alkylnaphthalene under more severe conditions.

Successive Alkylation. When aromatic compounds are alkylated in the presence of any catalysts, the hydrogen atoms are successively replaced, this yielding a mixture of products of varying degree of alkylation. For example, the methylation and ethylation of benzene proceeds until hexaalkylbenzenes are obtained:

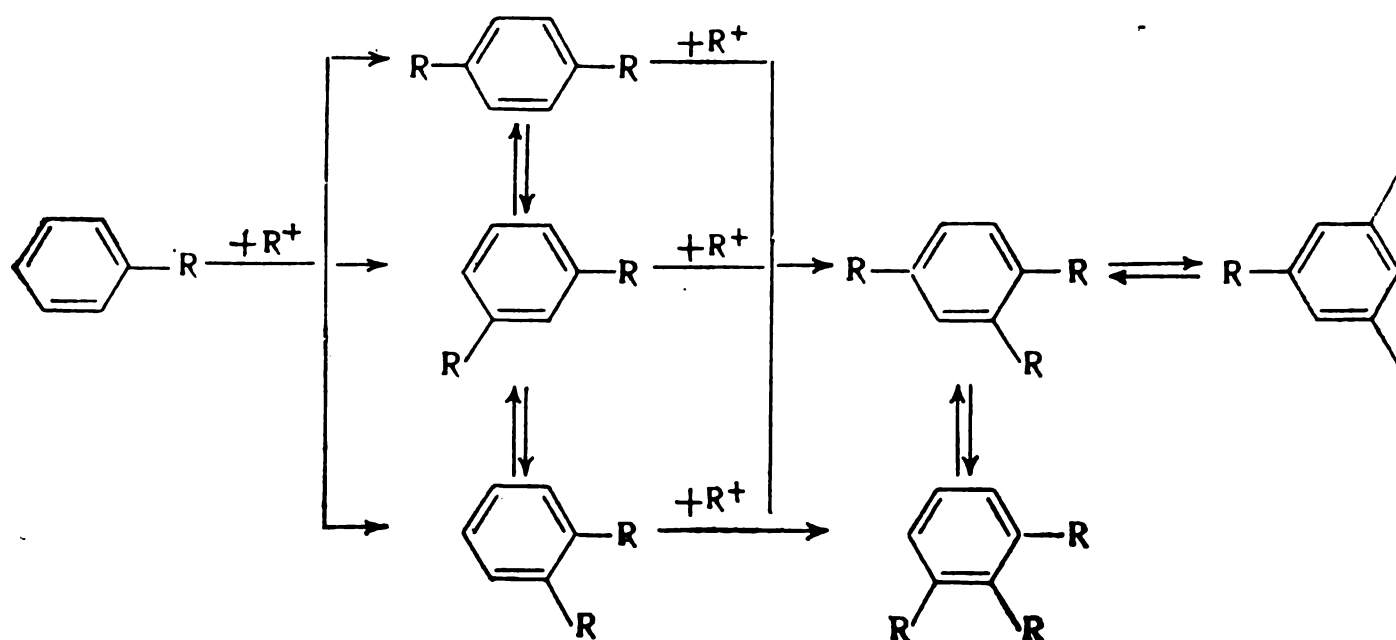


and the propylation goes on until *tetra*-isopropylbenzene is formed, etc.

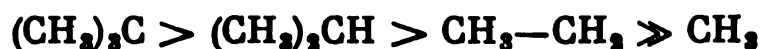
Each of the reactions is practically irreversible at moderate temperatures. For instance, the equilibrium constants for the synthesis of ethylbenzene from ethylene and benzene at 0, 200 and 500 °C. are, respectively, equal to 6×10^{11} , 2.2×10^4 and 1.9. However, on catalysis with aluminium chloride and under sufficiently severe conditions of catalysis in the presence of aluminosilicates and zeolites there takes place a reversible transalkylation (disproportionation) reaction involving an intermolecular migration of the alkyl groups:



The same catalysts are also used for the above-described reversible isomerization with an intramolecular migration of alkyl groups, as a result of which the *meta*-isomer predominates among dialkylbenzenes, the 1,3,5-isomer predominates among trialkylbenzenes, etc.:



The tendency of alkyl groups to migrate increases in the following order:



In the presence of an active aluminium-chloride complex these reactions proceed sufficiently rapidly even at room temperature, whereas for methylbenzenes additional heating is required.

Thus, on catalysis with proton acids or when other catalysts are used under milder conditions, the composition of alkylation products depends on kinetic factors; with aluminium chloride and under more severe conditions of catalysis with aluminosilicates and zeolites, there may arise, in the limit, an equilibrium composition of isomers and products of a successive alkylation reaction. This is very important for the choice of the optimal molar ratio of reagents for alkylation reactions which is determined by the cost of production of polyalkylbenzenes and recycling of excess benzene.

Under the kinetic regime of the process, since the second step of alkylation proceeds more rapidly than the first, at $k_2/k_1 = (1.2-2)$ the maximum content of monoalkylbenzene in the mixture is only 25-30 percent (molar). In order to increase the selectivity, the process has to be operated with the molar ratio of the alkylating agent to benzene being equal to $\beta_1 = (0.1-0.2)$ despite the high cost of the distillation and recycling of excess benzene to the reaction (Fig. 4.1a).

For the production of a monoalkylbenzene the equilibrium composition of the products of successive alkylation reactions is con-

siderably more profitable than the kinetic composition (Fig. 4.1b). For example, the equilibrium constant of the first of the transalkylation reactions given above is equal to about 4 for ethylbenzene and isopropylbenzene, which corresponds to the formation of a maximum amount of a monoalkylbenzene (about 50 mol percent). Besides, the by-product dialkylbenzenes formed can be recycled

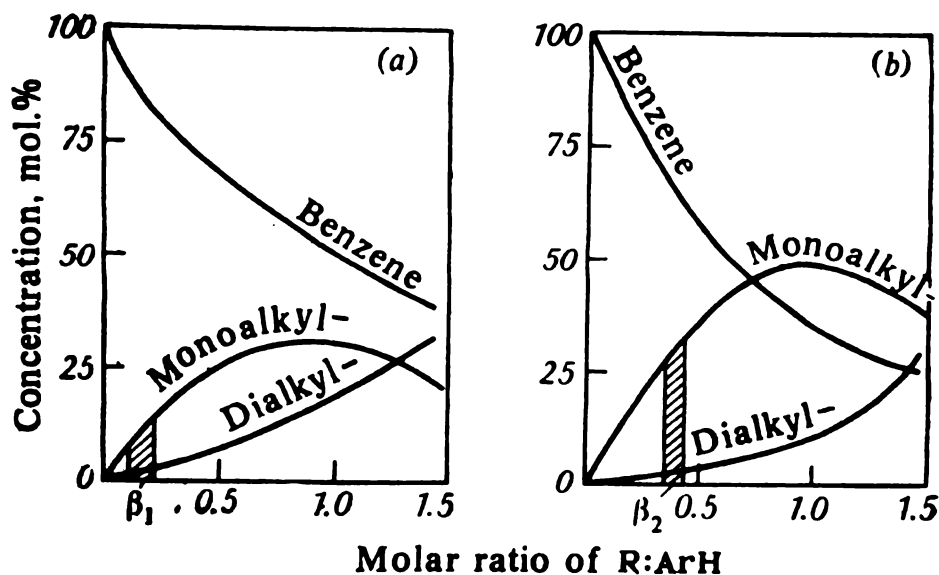


Fig. 4.1. Dependence of the composition of the reaction mass in alkylation of benzene on the ratio of the reagents:

a—irreversible alkylation; b—reversible alkylation.

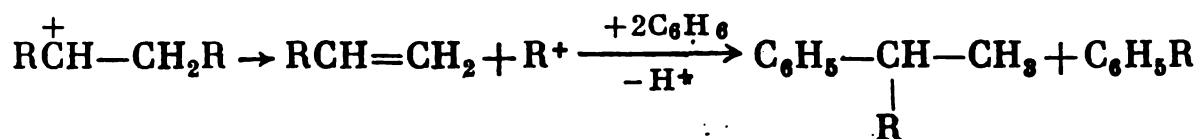
to the reaction to be converted to the end product upon transalkylation with benzene. All this increases considerably the selectivity and permits the process to be operated at a molar ratio of the alkylating agent to benzene equal to $\beta_2 = (0.30-0.50)$, thereby reducing the amount of excess benzene and the expenditure on its distillation and recycling.

Side Reactions. Apart from the formation of polyalkylbenzenes discussed above, formation of resins, decomposition of alkyl groups and polymerization of olefins are undesirable in alkylation reactions.

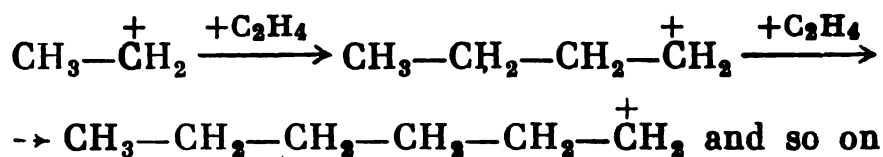
The resinification consists of the formation of condensed-ring aromatic compounds having high boiling points. Examples of such compounds formed in the alkylation of benzene are diarylalkanes, triarylindanes, diarylolefins. When naphthalene is alkylated, a larger amount of resins is formed, in which dinaphthyl and other compounds with condensed rings have also been detected. The formation of resins becomes especially significant with rise in temperature.

The same conditions lead to undesirable decomposition of alkyl groups and to the formation of by-product alkylbenzenes with a shorter alkyl group. For instance, by-product ethylbenzene is formed in the reaction involving propylene and toluene is formed as a by-product in the reaction with ethylene. Such decomposition of the alkyl group is especially pronounced in the alkylation effected by alkyl halides and olefins having a sufficiently long carbon chain.

The reaction presumably occurs at the step of splitting-off of the carbonium ion formed from the alkylating agent:



Finally, polymers are formed as a result of the successive interaction of the carbonium ion with an olefin (cationic polymerization):



The polymers have a low molecular mass and their formation is suppressed by the presence of an excess of an aromatic hydrocarbon with the olefin concentration in the liquid phase being reduced.

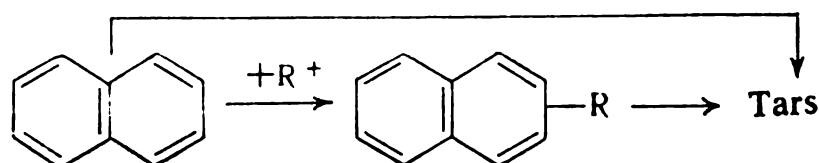
Process Kinetics. The alkylation reaction itself in the presence of an active aluminium chloride complex proceeds very rapidly, is strongly accelerated on agitation or intensive bubbling of gaseous olefins through the reaction mass and occurs in the diffusion region or a region close to it. Its velocity increases with increasing pressure, but it depends little on temperature because of the low activation energy. Here the usual dependence of the reactivity of olefins remains valid, it being stronger than the difference in their solubility. The rate-limiting step is presumably the diffusion of the olefin through the boundary film of the catalytic aluminium chloride complex, in which all the reactions take place. In contrast to this, transalkylation occurs at a much slower rate and is significantly speeded up with increasing temperature, since it has an activation energy of ≈ 63 kJ/mol (≈ 15 kcal/mol).

Both reactions are slowed down when the catalyst becomes gradually deactivated, but the velocity of the transalkylation reaction decreases especially strongly. As a result, a considerable amount of polyalkylbenzenes is accumulated in the reaction mixture; these polyalkylbenzenes have no chance to take part in the reversible transalkylation reaction. In order to avoid this, one has to reduce the supply of the reagents and, hence, the possibility of intensifying the process is limited by the slowest transalkylation reaction.

Apart from the reagent impurities, the deactivation of the catalyst is also favoured by the accumulation of some alkylation by-products, which are capable of strongly binding AlCl_3 or forming stable σ -complexes, which do not readily donate their protons to the olefin molecule. The by-products formed at low temperature, when transalkylation proceeds slowly, are polyalkylbenzenes and those formed at high temperature are polycyclic aromatic compounds and resins. It turns out that the optimal capacity and consumption of the catalyst in the production of ethylbenzene and isopropylbenzene

are attained at a certain average temperature ($\approx 100^\circ\text{C}$), when transalkylation occurs at a sufficiently fast rate and the amount of polycyclic compounds that deactivate the catalyst is still small.

In the synthesis of compounds with a longer alkyl group the choice of the temperature is limited by the side degradation reaction; when alkylnaphthalenes are produced, the limiting factors are condensation and resinification. In these cases, the optimal temperature range is $30\text{--}50^\circ\text{C}$; in the alkylation of naphthalene the selectivity can be additionally increased by using solvents. This is accounted for by the fact that in the sequence of reactions



the resinification is second order in naphthalene or alkylnaphthalene, and the principal reaction is first order. As a result, the selectivity with respect to alkylnaphthalene increases with decreasing naphthalene concentration.

4.2.2. Technology of the Alkylation of Aromatic Hydrocarbons

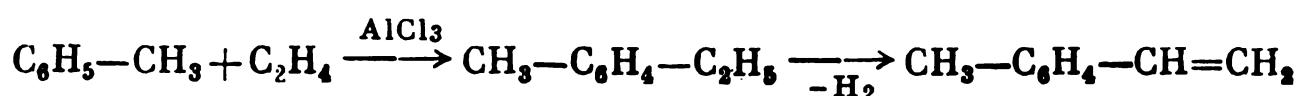
The multitonnage products of the alkylation of aromatic compounds are ethylbenzene and isopropylbenzene.

Ethylbenzene, $\text{C}_6\text{H}_5\text{—C}_2\text{H}_5$, is a colourless liquid which boils at 136°C . It is of industrial significance mainly because it is further converted to *styrene*, $\text{C}_6\text{H}_5\text{—CH=CH}_2$, which is one of the most important monomers for the manufacture of plastics and synthetic rubber. The cheapest ethylbenzene is obtained by deriving it from the xylene fraction of reforming or pyrolysis products, in which its content is 10–15 percent (page 76); the major source of ethylbenzene is the alkylation of benzene by ethylene in the presence of AlCl_3 .

Diethylbenzene, $\text{C}_6\text{H}_4(\text{C}_2\text{H}_5)_2$, which is formed as a by-product in this reaction and which is a mixture of the *meta*- and *para*-isomers, has assumed significance in the production of *divinylbenzene*, $\text{C}_6\text{H}_4(\text{CH=CH}_2)_2$, a valuable monomer for the manufacture of ion-exchange resins. High-quality diethylbenzene is obtained, however, by the transalkylation of ethylbenzene with AlCl_3 as catalyst:

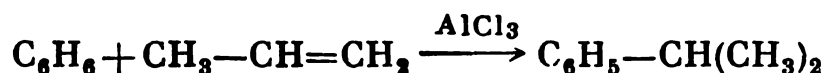


Just as with ethylbenzene, the alkylation of toluene gives *ethyltoluene*, which is dehydrogenated to yield *vinyltoluene*:



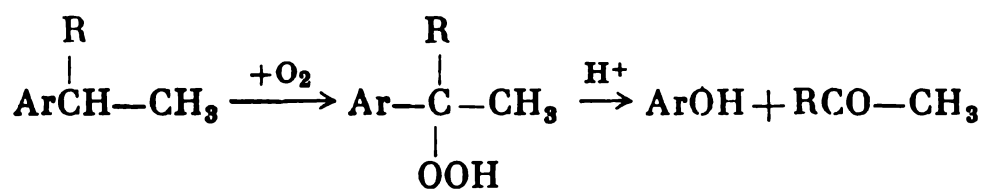
which may sometimes be used as a substitute for styrene, which is very important because of the shortage of benzene.

Isopropylbenzene, $C_6H_5-CH(CH_3)_2$, which is also known as *cumene*, is a colourless liquid (b.p. $152.5^\circ C$). It is obtained by the alkylation of benzene with propylene:



Isopropylbenzene was originally used as a high-octane additive to motor fuels; today its major consumer is the chemical industry.

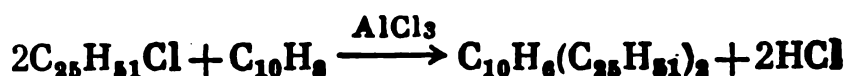
Isopropylbenzene is processed into α -methylstyrene, $C_6H_5-C(CH_3)=CH_2$ (a monomer for synthetic rubber) and, in especially large amounts, into cumene hydroperoxide, $C_6H_5-C(CH_3)_2-OOH$, which is used to produce phenol and acetone. In an analogous way, diisopropylbenzene goes to the production of dihydric phenols (hydroquinone and resorcinol) and isopropyltoluene is used to obtain cresols and acetone. 2-Isopropyl-naphthalene may be used as the feedstock for the synthesis of β -naphthol:



The alkylation of aromatics by isobutylene is employed on a smaller industrial scale; of its products mention should be made of *p-tert*-butyltoluene, $(CH_3)_3C-C_6H_4-CH_3$. It is further processed by way of oxidation to *p-tert*-butylbenzoic acid, which is of value for the production of lacquer resins and synthetic rubber.

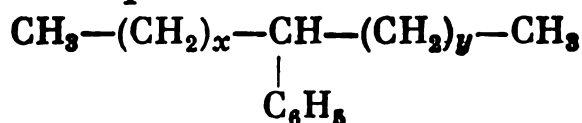
Of no less importance are alkylaromatic plasticizers, lubricating oils and additives obtained by the alkylation of aromatic compounds. The lubricating oils are synthesized by the alkylation (in the presence of $AlCl_3$) of naphthalene or mixtures of aromatic hydrocarbons extracted from petroleum fractions. The alkylating agents used are olefins (from ethylene to higher olefins obtained by the cracking of paraffin) or the chlorinated fractions of kerosene. With lower olefins, lubricating oils are synthesized by introducing 6 or 7 alkyl groups into the naphthalene molecule; the number of alkyl groups with higher olefins ranges from 2 to 4.

The lubricating-oil additives produced by the alkylation of aromatics are used for various purposes. For example, "Paraflow" is synthesized from a monochloroparaffin and naphthalene; it is added to lubricating oils to reduce their pour points (such compounds are known as *pour-point depressants*):



Synthetic plasticizers (softening agents) for rubbers are produced in the same way from the same starting compounds.

Alkylbenzenes with a rather long alkyl group are intermediates for the production of surfactants and detergents of the type of *sulphonols*, $\text{RC}_6\text{H}_4\text{SO}_2\text{ONa}$, which result from the further sulphonation of alkylbenzenes and neutralization. The feedstocks used in the past to produce such alkylbenzenes were low-molecular-mass polymers and copolymers of propylene with butylenes (page 60), but because of their branched structure the resulting surfactants were poorly biodegradable. Therefore, at present the following alkylating agents are used: (1) monochloroparaffins obtained by the chlorination of dearomatized fractions of kerosene or soft paraffin waxes derived from them in one or another way; and (2) α -olefins with a straight carbon chain produced by the thermal cracking of paraffin or by organoaluminium synthesis. Because of the isomerization in the presence of AlCl_3 the alkylate is a mixture of *sec*-alkylbenzenes with different positions of the aromatic ring:



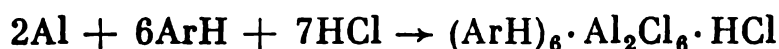
Besides, it contains disubstituted products ($\text{C}_6\text{H}_4\text{R}_2$), and in the alkylation by a monochloroparaffin obtained from an insufficiently pure feedstock there are also present *tert*-alkylbenzenes and cycloalkylbenzenes.

Starting Materials. Technical benzene or any other aromatic hydrocarbon used for alkylations must first be dried, for which purpose the water is distilled off in the form of an azeotrope with an aromatic hydrocarbon (benzene or toluene). In this azeotropic drying operation the moisture content drops to 0.002-0.005 percent. Fractions of lower olefins are supplied from the gas-separating pyrolysis or cracking units in a sufficiently dry state, but not infrequently they contain various impurities, this leading to an increased consumption of the reagents and catalyst and also to the formation of by-products; it is sometimes difficult to purify the end products from the by-products formed (C_2H_2 or its homologues, butadiene, other olefins). In some cases, the end product is not freed from these compounds, the tolerable content being 2-3 percent (by volume); much better results are obtained when the amount of such impurities is reduced by a factor of about 10. A more complete purification of the fractions from unsaturated compounds is not required for alkylations; this applies to a greater extent to paraffinic impurities. The optimal degree of purification of fractions must evidently be governed by economic calculations.

Aluminium chloride is introduced into the reaction in the form of a liquid catalytic complex, which is prepared in a stirred slightly heated vessel from technical AlCl_3 , diethylbenzene or approxi-

ately equal amounts of benzene and a dialkylbenzene (the complex cannot be obtained from benzene alone); a small amount of a chloro derivative (say, C_2H_5Cl) or water is added. Where anhydrous HCl is available it may also be used to prepare the complex.

It has been lately recommended to prepare the complex in a centralized way—from wastes of metallic aluminium, aromatic hydrocarbons and anhydrous HCl :



The Reaction Unit. The batch process is operated in a stirred reactor fitted with a cooling jacket and sometimes with a coil. Benzene and $AlCl_3$ or a catalytic complex (10-20 percent by volume

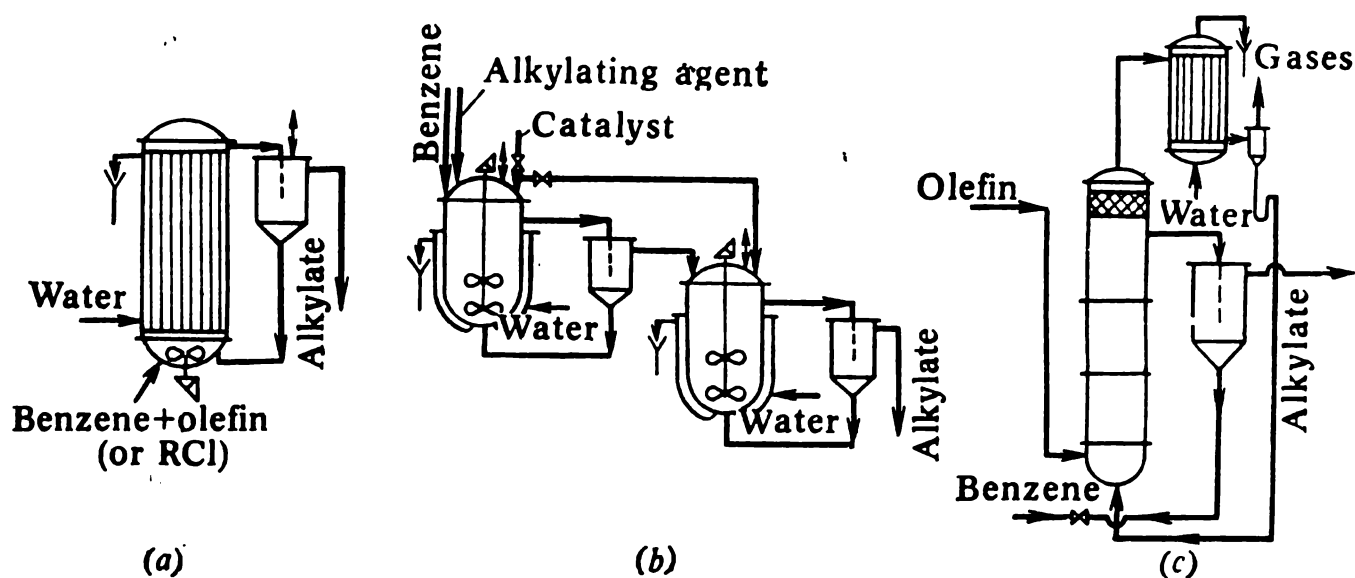


Fig. 4.2. Reaction units for the alkylation of aromatic hydrocarbons in the presence of aluminium chloride:

a—tubular reactor; b—cascade of stirred reactors; c—column-type reactor.

of the reaction mass) are charged into the reactor, following which the liquid olefin or chloro derivative is added on stirring and the required temperature is maintained. The switch to the continuous process is effected when use is made of liquid alkylating agents by two principal methods.

In one method, a tubular reactor is used (Fig. 4.2a), the lower part of which is fitted with a powerful stirrer, which emulsifies the reaction mass. The reagents and the catalytic complex, which has settled in the separator, are introduced into the lower part of the reactor and the emulsion formed moves upwards through the pipes and is cooled with the water flowing in the intertube space. In the separator, the hydrocarbon layer is separated from the catalytic complex and then sent to refinery. The residence time of the mixture in the vessel must be such as to provide the completion of the reaction.

carrying out the continuous operation involving agents consists of the use of a cascade of 2-4 (Fig. 4.2b). The reagents are introduced into the reaction mass overflows through the side pipe into which it has passed through the separator; in the process, benzene is separated and returned to the reactor. This is accounted for by the fact that in a single stage it is difficult to prevent the loss of the alkylating agent, which is the major product. The residence time of the cascade at a reaction temperature of 40-60 °C is being dictated by the conditions of heat recovery to approach the equilibrium, which is favourable for monoalkylated compounds.

The alkylation of aromatic hydrocarbons by gaseous olefins is carried out in vertical columns (Fig. 4.2c), the inner surface of which is protected against corrosion by acid-resistant sheets. The columns are filled with a liquid, which fills the column up to the overflow. This liquid is a catalytic AlCl_3 complex (20-40 percent by weight) in a mixture of aromatic hydrocarbons insoluble in it.

The olefin fraction are introduced into the lower part of the column; the olefin fraction bubbles through the liquid. The liquid reaction mass overflows through the side pipe into a separator, where the heavier catalytic complex is separated and returned to the bottom of the alkylator, and the olefin fraction is sent to further processing.

The benzene is removed practically only by the heating of the reaction mixture by the evaporation of the benzene. The benzene in the effluent gases enter the reflux condenser, where it is condensed and returned to the alkylator; the olefin fraction is sent to further processing. Hence, autothermal alkylation is carried out in the alkylator and the temperature of the reaction is maintained by the pressure used and the amount of effluent gases (depending on the starting olefin fraction).

The reaction mixtures are charged into the reactor, not at a pressure of up to 0.5-0.6 MPa is employed in order to ensure the recovery of benzene from the off-gases. The temperature in the alkylator reaches 130-140 °C, which leads to the formation and a deactivation of the catalyst. In order to reduce the pressure to 0.15-0.2 MPa, a moderate amount of off-gases, when the temperature is at an optimal level, at about 100 °C.

The Process. Figure 4.3 shows the flow diagram for the alkylation of ethylbenzene and isopropylbenzene by the reaction with a gaseous olefin in the presence of AlCl_3 . The benzene, together with the benzene returned at the separator, is sent into column 3, which is designed for drying

The gases leaving the condenser 10 contain a considerable amount of the vapours of low-volatile benzene (especially when dilute olefin fractions are used). In order to recover the benzene these gases are sent to absorber 13, which is refluxed by the polyalkylbenzenes separated from the reaction mass at the separation stage. The solution of benzene in polyalkylbenzenes accumulated in the lower section of the absorber is run into reaction unit 9 for transalkylation. The gases leaving absorber 13 are washed by water in scrubber 14 to remove HCl and are discharged into the atmosphere or used as a flue gas.

The hydrocarbon layer leaving separator 12 consists of benzene and mono- or polyalkylbenzenes. It also contains a small amount of other benzene homologues formed by the olefin impurities present in the starting fraction or by partial decomposition of the alkyl group under the action of AlCl_3 . In the synthesis of ethylbenzene and isopropylbenzene the reaction mass contains 45-55 percent (by weight) of benzene, 35-40 percent (by weight) of monoalkylbenzene, 5-12 percent (by weight) of dialkylbenzene and up to 3 percent (by weight) of higher alkylated compounds, by-products and tars. The entire mixture passes through water cooler 15 and is settled additionally in cold separator 16, from which the catalytic complex is periodically returned to the alkylator. The alkylate is then sent to purification from the dissolved hydrogen chloride and traces of aluminium chloride. To do this, the mixture is washed in a system of counterflow columns 17 and 18 first by water and then by aqueous alkali. The neutralized hydrocarbon mixture (the alkylate) is run over fractional distillation.

The reaction products are separated in several continuous fractionating columns (not shown in Fig. 4.3). The benzene and the water, which has been dissolved in hydrocarbons at the washing stage, are distilled off in the first column. In the next column, the fraction containing mainly the major product with the nearest benzene homologues present as impurities is distilled in vacuum. It is then subjected to additional fractionation in order to isolate technical ethylbenzene or isopropylbenzene. The still liquid of the second column contains polyalkylbenzenes containing an impurity of tars formed by the action of AlCl_3 . The polyalkylbenzenes are distilled off in vacuum from tars and are used for the absorption of the benzene from the exit gases and for the preparation of the catalytic complex. The polyalkylbenzenes are again returned through these intermediate operations to unit 9, where they are subjected to dealkylation. The yield of the end product reaches 94-95 percent with account taken of all the losses (the amount of AlCl_3 consumed per 1 ton of monoalkylbenzene is about 10 kg).

The alkylation technology described above has a number of drawbacks and has been lately improved. For example, the forma-

tion of a large amount of waste waters can be eliminated by decomposing the acid alkylate by a small quantity of water; this gives a concentrated solution of AlCl_3 hexahydrate, which finds various applications. It has also been suggested that the alkylation of benzene and the transalkylation of polyalkylbenzenes, which occur at different velocities, be conducted in different units, which reduce

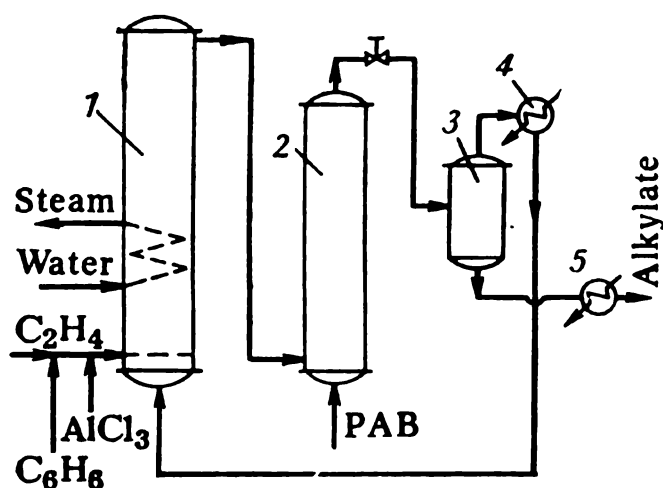


Fig. 4.4. Flow diagram for homogeneous alkylation of benzene:

1—alkylator; 2—transalkylator; 3—separator; 4—condenser; 5—cooler.

the recycle and energy consumption and enables the operation to be effected in a smaller excess of benzene with respect to the olefin.

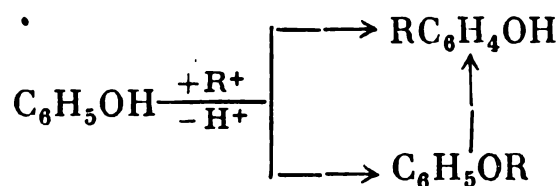
One of the variants of the modified alkylation process consists of the use of a small amount of the catalytic complex dissolved in the alkylate (homogeneous alkylation). Here, because of the absence of large masses of the catalyst, the reaction is effected at 160-200 °C, the pressure being such as to keep the mixture in the liquid state. Ethylene, benzene and a small quantity of the

catalytic complex are charged into alkylator 1 (Fig. 4.4); the heat evolved is removed by the boiling water condensate with the process steam being produced (this heat is not used in the ordinary technology). The resulting alkylate passes into transalkylator 2, into which polyalkylbenzenes (PAB) are run from the separation stage they give with benzene an extra amount of the end product. The alkylate from unit 2 is throttled to atmospheric pressure and the energy released is utilized for the vaporization of some of benzene which is condensed and returned to alkylation. The liquid alkylate from separator 3 is cooled and led to neutralization and further separation. Several plants are now operating according to this technology.

4.2.3. Alkylation of Phenols

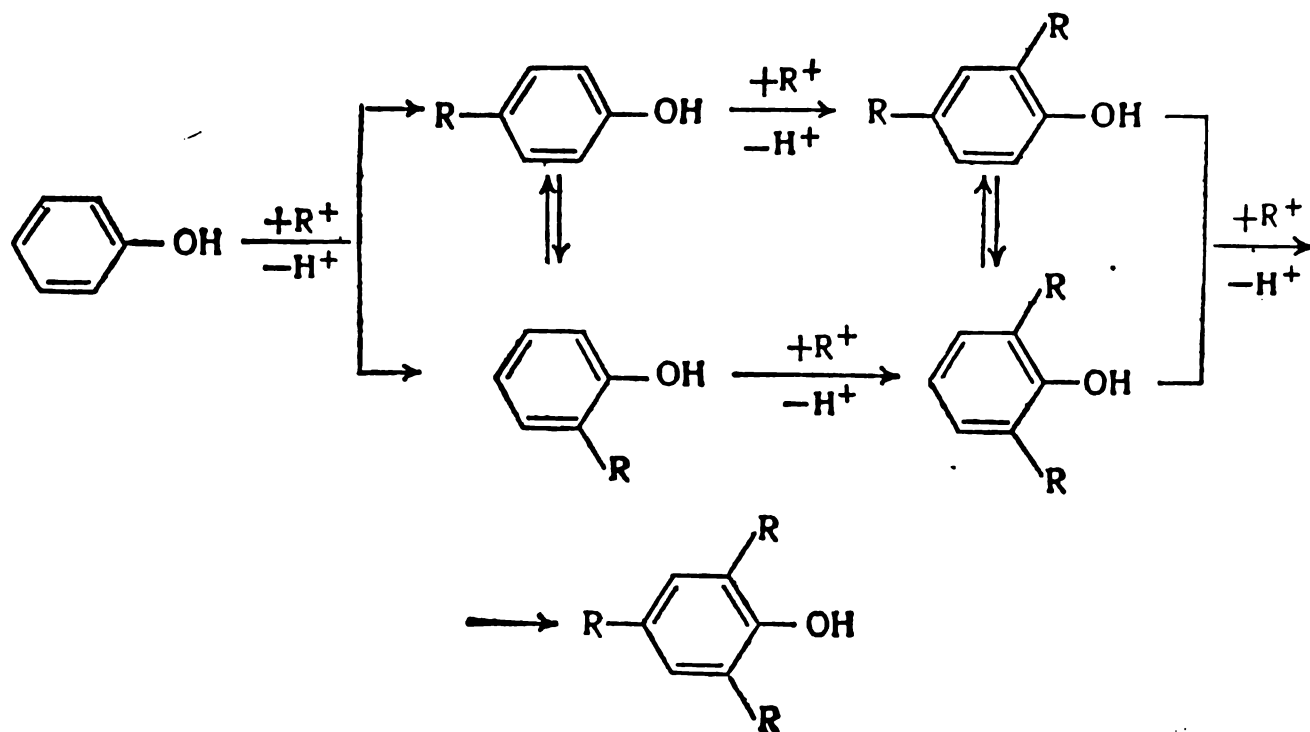
Phenols form with AlCl_3 inactive salts (ArOAlCl_2), which is why proton acids or metal-oxide acid-type catalysts are used for the alkylation of phenols. This makes it possible to employ only alcohols and olefins as alkylating agents. Apart from the nuclear-substituted products, there is obtained a small amount of ethers of phenol, which readily undergo rearrangement to alkylphenols.

nols:



It has been found that alkylphenols are predominantly formed by direct alkylation in the ring. The mechanism of this reaction is analogous to that described earlier for aromatic hydrocarbons; the hydroxyl group of phenols strongly activates the 4 and 2 positions in the complete absence of *meta*-isomers in the products.

The alkylation occurs consecutively with the formation of mono-, di- and trialkylphenols, but there also takes place an acid-catalyzed rearrangement involving the migration of *ortho*-alkyl groups with the formation of *para*-isomers, which in this particular case are thermodynamically most stable. Thus, the scheme of conversions for the alkylation of phenol is as follows:



When the reaction is catalyzed by protic acids, the *para*-isomer predominates among the monoalkylphenols, but when the catalyst activity, temperature and reaction time are increased, the amount of this isomer may increase from 60-80 to 95 percent upwards because of the isomerization of the *ortho*-isomer. Among the disubstituted phenols, 2,4-dialkylphenol always predominates considerably and its proportion increases even more under the conditions indicated above.

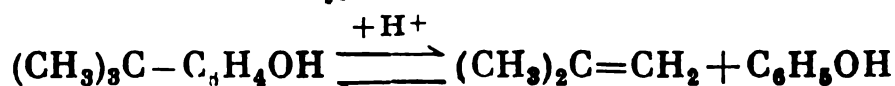
In contrast to the alkylation of aromatic hydrocarbons, when alkyl groups are introduced successively, the first step proceeds faster than the second and the last step faster than the third. The composition of the products formed by successive substitution is

also influenced by the reversible transalkylation reaction:



The equilibrium of this reaction is shifted to the right. Therefore, the content of monoalkylphenol may increase in the mixture obtained with increasing catalyst activity, temperature and reaction time. For example, as compared with the alkylation of benzene (Fig. 4.1), the maximum amount of monoalkylphenol under the kinetic regime is ≈ 50 percent (molar); in a state close to the equilibrium it reaches 75-80 percent (mol). When monoalkylphenols are synthesized as the end products, this allows the operation to be carried out with a relatively small excess of phenol with respect to the olefin [$\beta = (0.8-0.95)$] and even with their equimolar amount. The selectivity increases even more when the dialkylphenols formed as by-products are subjected to transalkylation with phenol according to the scheme given above. Conversely, when the end products are dialkylphenols, an excess of olefin is used, which depends on the ratio of the reaction rates and the thermodynamic factors in the subsequent reaction steps.

Apart from ethers of phenols and polyalkyl-substituted phenols, the alkylation by-products also include polyolefins and the alkylphenols formed from them, which have a longer alkyl group. Conversely, when higher (especially, branched) olefins are used in reactions, they are depolymerized to give alkylphenols with a shorter alkyl group. The general method used to suppress these side reactions is to lower the temperature, since alkylation has the lowest activation energy (≈ 21 kJ/mol or 5 kcal/mol). To prevent the polymerization of the olefin, it is also necessary to reduce its concentration in the liquid, this being achieved by gradually introducing olefins into the reaction mass. Finally, it should be noted that the reactions of phenols with isoolefins are appreciably reversible, and the heating of the corresponding alkylphenols in the presence of an acid catalyst leads to the formation of an olefin:



Evidently, this reaction is partly responsible for the occurrence of isomerization and transalkylation.

The catalyst (a protic acid) most frequently used on an industrial scale is sulphuric acid. It is most active among other available and inexpensive acids, but it catalyzes more strongly the side reactions, leading additionally to the sulphonation of phenol and to the sulphation of the olefin; these reactions yield phenolsulphonic acids, $HOC_6H_4SO_3OH$, and monoalkyl sulphates, $ROSO_3OH$, which also become involved in the catalysis of the process. In the presence of sulphuric acid the alkylation by *n*-olefins (except ethylene)

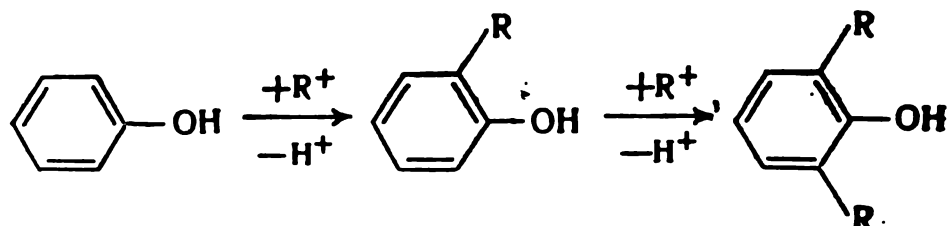
proceeds at 100-120 °C, and with more reactive isoolefins and styrene the reaction occurs at as low a temperature as 50 °C; however, in order to speed up the process, in the latter case the alkylation is also effected at ≈ 100 °C using H_2SO_4 in an amount of 3-10 percent by weight). Another catalyst, which does not cause side sulphonations and which is milder in its action is *p*-toluenesulphonic acid, $\text{H}_3\text{C}_6\text{H}_4\text{SO}_2\text{OH}$. But this compound is less active and more expensive as catalyst than H_2SO_4 .

In the presence of these catalysts the alkylation of phenol proceeds as a homogeneous reaction according to the following kinetic equation:

$$r = k [\text{H}^+][\text{Olefin}][\text{ArOH}]$$

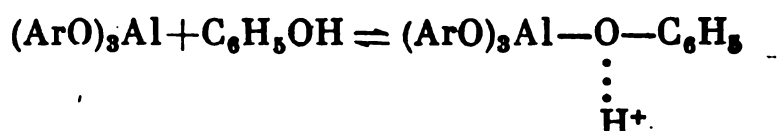
A drawback common to these catalysts is the necessity to wash the acid catalyst, as a result of which a considerable amount of toxic waste waters is formed. Therefore, heterogeneous catalysts have attracted attention and found practical application, especially cation-exchange resins, which are separated from the reaction mass by simple filtration. With the cation-exchange resin KU-2 the alkylation of phenols by isoolefins occurs at 120-140 °C, though at a slower rate than in the presence of sulphuric acid.

Wide use has recently been made of the *ortho*-alkylation of phenols, which proceeds in the presence of aluminium phenolates, $(\text{ArO})_3\text{Al}$, as catalysts. Here, even with the *para*-position being unoccupied the alkyl group is directed to the *ortho*-position with the successive formation of mono- and dialkylbenzenes:



With isoolefins the reaction occurs even at ≈ 100 °C; as the temperature increases the *para*-alkylation becomes more and more appreciable.

The use of aluminium phenolate as catalyst is accounted for by its structure, it being an aprotic acid capable of forming with phenol a complex having high acidity:

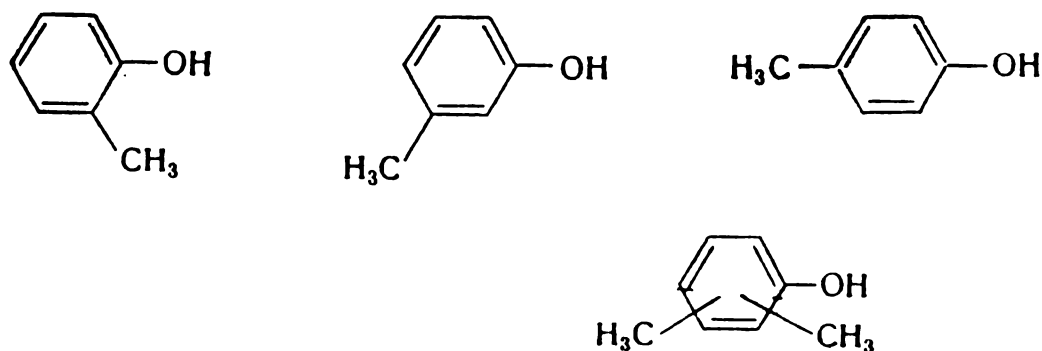


It is believed that an olefin forms with a proton a carbonium ion, which is not released into the bulk and attacks the nearest *ortho*-position of phenol in an intracomplex reaction.

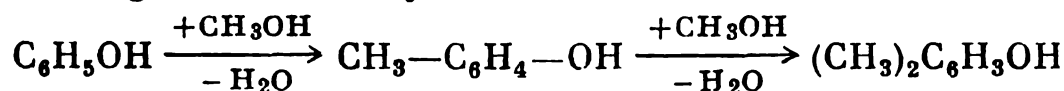
The gas-phase alkylation process characterized by analogous kinetic regularities is applicable only for the methylation of phe-

nol by methanol. It is effected in the presence of a heterogeneous acid-type catalyst (aluminium oxide, aluminosilicates, etc.). At 200-290 °C there are mainly produced *o*-cresol, xlenols and anisole but at a higher temperature (350-400 °C), according to what has been said above, the yield of *p*- and *m*-cresols increases and that of anisole and xlenols decreases.

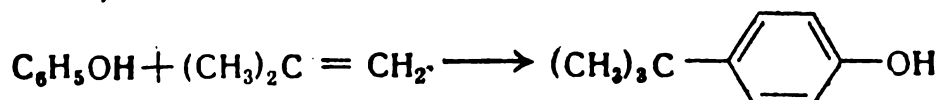
Products. The simplest homologues of phenol: *o*-, *m*- and *p*-cresols and the isomeric xlenols



are present in coal coking products, but their amount is very small and cannot meet the demands in the production of polymeric materials, pesticides, antioxidants, etc. One of the routes to their synthesis that has been realized on an industrial scale in a number of countries is the vapour-phase methylation of phenol by methanol over a heterogeneous catalyst:

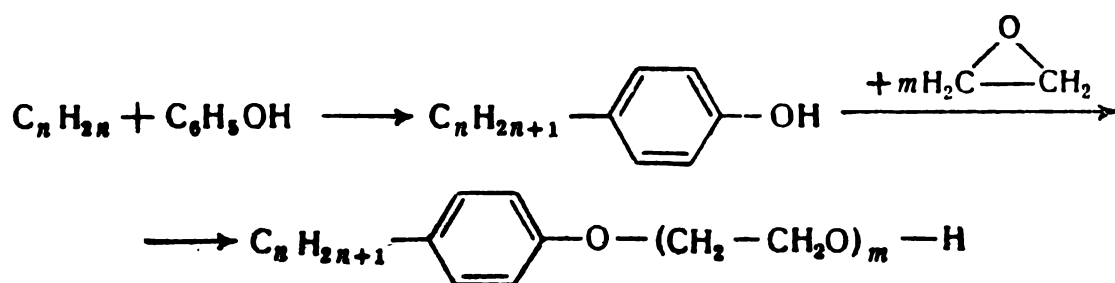


Of the monoalkylphenols, *p*-*tert*-butylphenol obtained from phenol and isobutylene is of industrial value:



When it is added to phenol upon polycondensation with formaldehyde there are formed difficultly soluble polymers, which is of significance for their use as paint and varnish coatings.

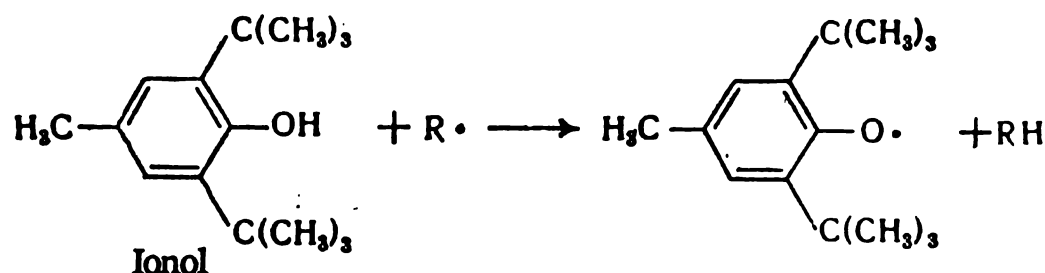
Monoalkylphenols with an alkyl group of 5-8 carbon atoms are strong bactericides; with a longer alkyl group (up to 8-12 carbon atoms) they are valuable intermediates in the synthesis of nonionic surfactants by way of their oxyethylation:



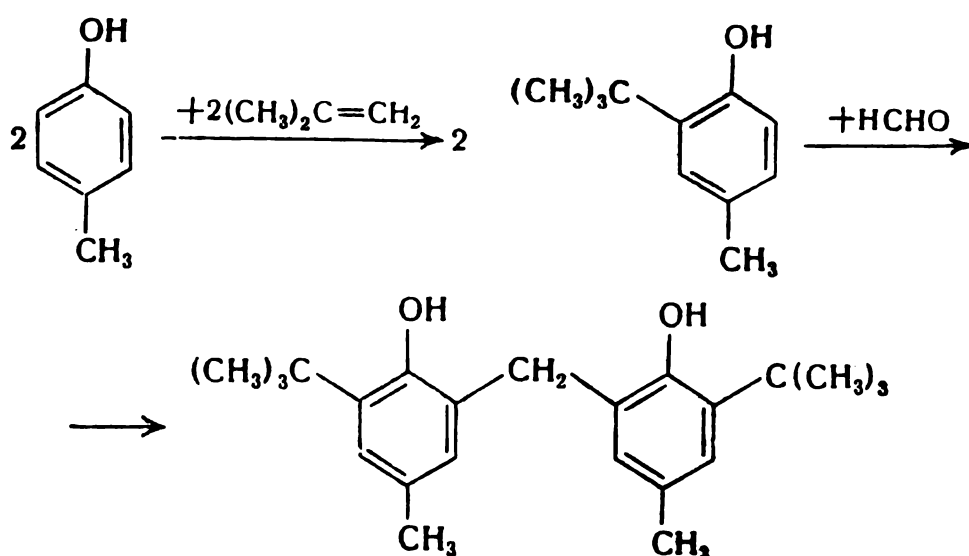
The alkylating agents used are low-molecular-weight polymers and copolymers of olefins (diisobutylene, propylene trimer and

tetramer, copolymers of butylene with amylenes, etc.), which give *tert*-alkylphenols. In order to obtain products that are better biochemically degradable, it is expedient to use *n*-olefins.

The most important consumer of alkylphenols and products of their further conversion is the production of stabilizers which are incorporated into polymers and lubricating oils to protect them from thermal degradation, which occurs gradually when these materials are used, especially at elevated temperatures. The degradation occurs by a radical-chain mechanism; it can be inhibited by using various compounds capable of binding free radicals or rendering them unreactive. Alkylphenols give rise in this process to inactive radicals stabilized through the conjugation with the aromatic ring; an especially strong effect is manifested by phenols with two branched groups in the *ortho*-position, when the effect of conjugation is supplemented by the spatial effect of the bulky substituents:

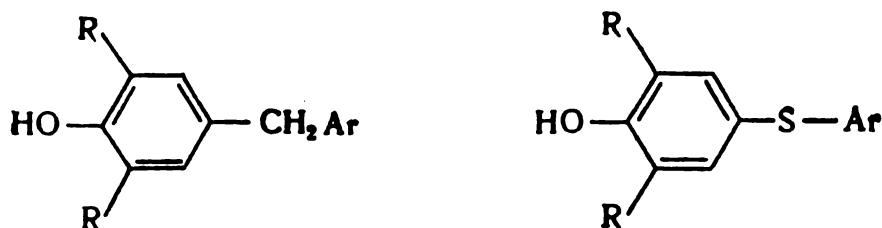


The first formula belongs to one of the most popular stabilizers—*ionol*, which is produced from *p*-cresol and isobutylene. The antioxidant-2246 produced by the condensation of *o*-*tert*-butyl-*p*-cresol with formaldehyde is used for the same purpose:



but their common shortcoming is the limited raw-material source, this being a consequence of a shortage of cresols. It is because of this that the *ortho*-alkylation reaction has become an important industrial process, which allows the use of more readily available phenol as the feedstock. Most stabilizers of this type belong to dihydric compounds with methylene or sulphide bridges between 2,6-

dialkylphenol (obtainable from isobutylene, styrene, etc.) and any aromatic hydrocarbon (mesitylene, durene) or another alkylphenol:



Process Technology. The alkylation of phenol is often operated batchwise. When high-boiling liquid olefins are used, the reaction is carried out in a stirred vessel fitted with a jacket for steam heating or water cooling. Phenol and the catalyst are charged into the apparatus and heated up to 90 °C; after they are stirred and cooled the liquid olefin (diisobutylene, propylene trimer or tetramer, styrene) is introduced. But during the second half of the reaction the reaction mass must be heated. The operation lasts for 2-4 h. Then the reaction mass is neutralized in a mixer with 5-percent caustic, the amount of which is equivalent to that of the acid catalyst, the mixture is heated by open steam. The unreacted olefin is distilled off, separated from the water (after its vapours are condensed) and may be reused for the alkylation. The neutralized organic layer of crude alkylphenols is separated from the aqueous solution of salts and sent to vacuum distillation, where the water, residual olefin and unconverted phenol are distilled off.

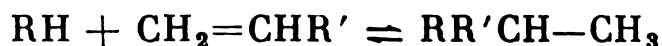
When alkylphenols are produced from gaseous olefins, it is expedient to use, instead of a stirred reactor, a hollow column, where the reaction mass is agitated by bubbling the olefin. The heat of the reaction can be removed by means of internal or external coolers. In order to switch over to the continuous operation, which intensifies the process and improves the composition of the reaction mass, it is more profitable to use a cascade of the reactors described above, just as in other irreversible consecutive-parallel reactions.

In the new process of phenol alkylation in the presence of ion-exchange resins the catalyst is suspended in the liquid present in the reaction column. Phenol and an olefin are introduced into the bottom of the column. At 120-140 °C over the KU-2 resin or at 150-160 °C over aluminosilicate the feed volume velocity is about 0.15 h⁻¹. The reaction mass is filtered off from the catalyst particles and is sent to distillation. The consumption of the catalyst is only 0.4 percent (by weight) based on the amount of alkylphenols produced.

4.2.4. Alkylation of Paraffins

This process is intended for the synthesis of high-octane motor fuels and has found wide application in all developed industrialized countries, including the USSR.

The alkylation of paraffins by olefins is an equilibrium exothermic process, which is the reverse of the cracking of hydrocarbons:



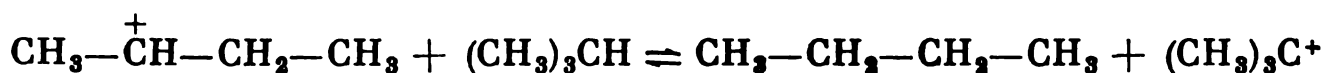
The thermodynamic relationships for this reaction have already been discussed in Chapter 1 in connection with the cracking process. Evidently, the equilibrium of the reverse reaction of paraffin alkylation is shifted to the right with decreasing temperature and at 100 °C and lower temperatures the reaction may be considered to be practically irreversible. It is exactly under such conditions that the catalytic alkylation of isoparaffins is accomplished on an industrial scale.

The catalysts used for the alkylation of paraffins by olefins are the same acid catalysts that are employed for the alkylation of aromatic compounds—aluminium chloride, anhydrous hydrogen fluoride and sulphuric acid. Sulphuric acid is used most often.

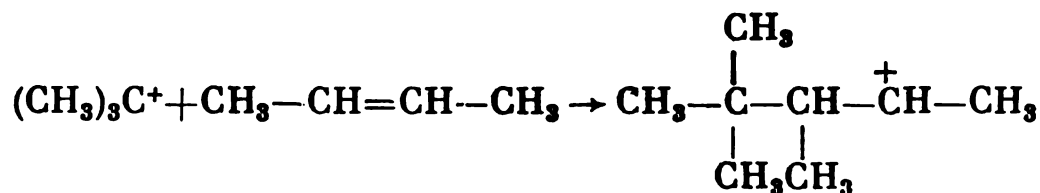
Among paraffins only isoparaffins with a tertiary carbon atom are capable of undergoing catalytic alkylation. Various olefins may be used (even ethylene), but those employed most often are *n*-butylenes, which alkylate isobutane with the formation of C_8H_{18} hydrocarbons, whose boiling point makes them most suitable as a component of motor fuels.

The structure of products obtained by the catalytic alkylation of isoparaffins does not usually correspond to that expected from the structure of the starting compounds. For example, the interaction of *n*-butylene with isobutane gives a mixture of 2,2,4-, 2,3,4- and 2,3,3-trimethylpentanes. The first isomer, called isooctane, is the reference standard in the scale of octane numbers—the octane number for isooctane is assumed to be equal to 100.

The cause for the difference in the structure of the products lies in the specificity of the reaction mechanism, which is complicated by isomerization processes. The secondary carbonium ion formed from an *n*-olefin is less stable than the tertiary carbonium ion, this being responsible for a fast exchange of the hydride ion with isoparaffin:

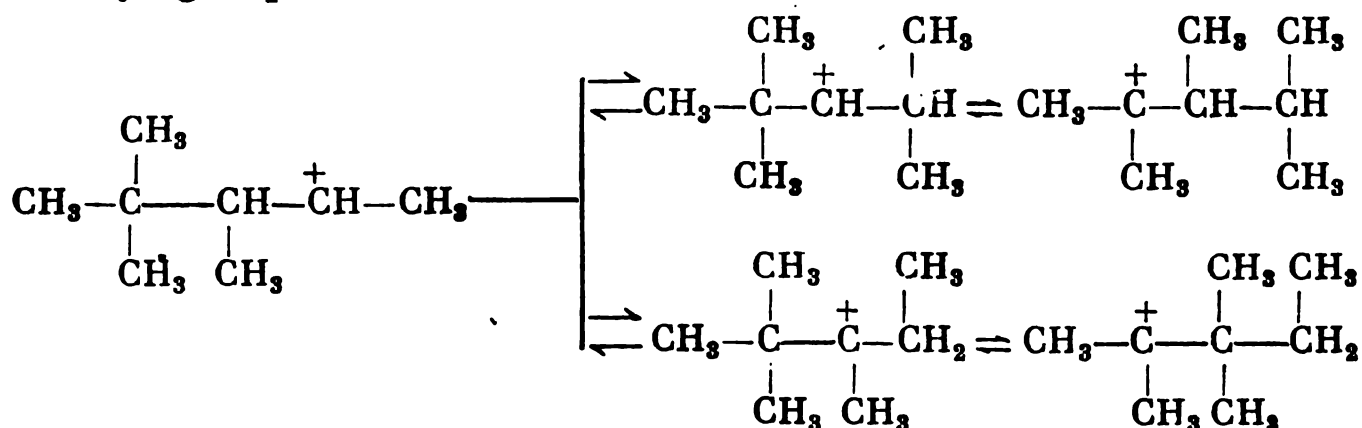


The *tert*-butyl cation formed interacts then with the starting olefin:

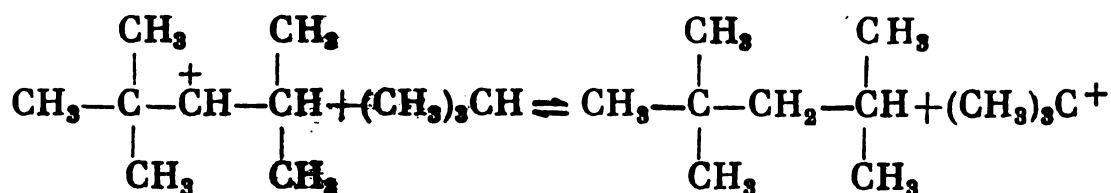


The resulting carbonium ion is liable to undergo intramolecular rearrangements accompanied by the migration of hydrogen and

methyl groups:

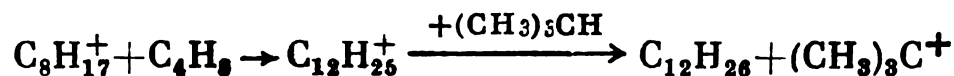


These carbonium ions react with the isobutane to yield the hydrocarbon C_8H_{18} and *tert*-butyl cation:



which provides the occurrence of an ionic-chain process. The composition of the isomers depends both on the stability of the intermediate carbonium ions and on the rate of their exchange reaction with isobutane.

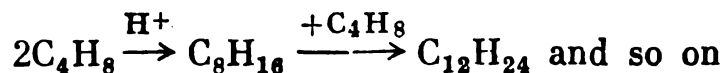
Evidently, the isooctyl cations formed as intermediates are also capable of undergoing a reaction with olefins:



Such is the route taken by the consecutive-parallel alkylation reactions; in order to suppress the formation of higher hydrocarbons an excess of isoparaffin with respect to the olefin is required.

The resultant alkylates are found to contain lower and higher paraffins with a number of carbon atoms being not a multiple of that of the reagents. For example, when isobutane is alkylated by butylenes, the alkylate contains 6-10 percent of C_5 - C_7 hydrocarbons and 5-10 percent of C_9 and higher hydrocarbons. It is obvious that they may appear only as a result of decomposition processes, which are favoured by a rise in temperature.

A further side reaction is the cationic polymerization of the olefin:



which yields low-molecular-weight unsaturated polymers, which somewhat impairs the quality of the alkylate and causes an increased consumption of the catalyst.

The use of an excess of isoparaffin suppresses all side reactions and has a positive effect on the yield of the alkylate, the content of

the end fraction in it, its octane number and the consumption of the catalyst. Since too large an excess of isoparaffin requires additional expenditure on its regeneration, there has been found an optimum excess which corresponds to a molar isoparaffin-olefin ratio of 4 : 1 to 6 : 1 in the starting mixture.

The alkylation temperature is chosen so as to suppress as much as possible the side decomposition and polymerization reactions and to maintain a sufficiently high reaction velocity. When the reaction is catalyzed by sulphuric acid, it is carried out at 0-10 °C; in the presence of anhydrous hydrogen fluoride the reaction is conducted at 20-30 °C under some pressure. The alkylation of isobutane by ethylene in the presence of AlCl_3 is accomplished under pressure at 50-60 °C.

4.2.4.1. Technology of Isoparaffin Alkylation

The feedstock most often used on an industrial scale is isobutane; isopentane is employed much more seldom. Of olefins, the most frequently used alkylating agents are *n*-butylenes (a mixture of 1- and 2-isomers), which with isobutane give an alkylate which is rich in C_8 hydrocarbons and which is often simply called isooctane. The feedstock used in some cases is a butane-butylene fraction of cracked gases containing all the required reagents and freed from butadiene.

The reaction mass is a two-phase system, which is emulsified by means of stirrers or feed pumps. When sulphuric acid is used as catalyst, its concentration is important. Best results are obtained with 98-100 percent acid, but it is gradually diluted with the moisture present in the reagents. The minimum permissible concentration is 88-90 percent, which is why part of sulphuric acid has to be removed from the system and fresh sulphuric acid added. The consumption of sulphuric acid is usually 5-7 kg per 100 litres of alkylate. In the reactor itself the volume acid-to-hydrocarbon ratio is about 1 : 1 and amounts even to 70 percent (by volume) of acid. The excess catalyst is separated from the hydrocarbons in the separator and returned to the reaction.

Two types of vessels are used for the process in which the heat evolved is removed in different ways—by internal cooling with liquid ammonia (or propane) or by way of evaporation of excess isobutane. In the first case, in the alkylator fitted with a powerful stirrer there are cooling pipes, in which the heat-exchange medium is evaporated (see Fig. 4.2a). Its vapours are then sent to a cooling unit, where they are again converted to the liquid.

More effective is the removal of heat by evaporation of excess isobutane, which facilitates the control of temperature. One of the interesting types of alkylators operating according to this prin-

ciple is shown schematically in Fig. 4.5 (unit 4). In it the reaction space is divided by partitions into several sections fitted with stirrers (cascades). Butylene is supplied separately into each section, as a result of which the olefin concentration in the sections is very low and this enables the side polymerization reaction to be suppressed. Sulphuric acid and isobutane are led into the first section from the left and the emulsion overflows through the vertical partitions from one section to another. The second section from the right

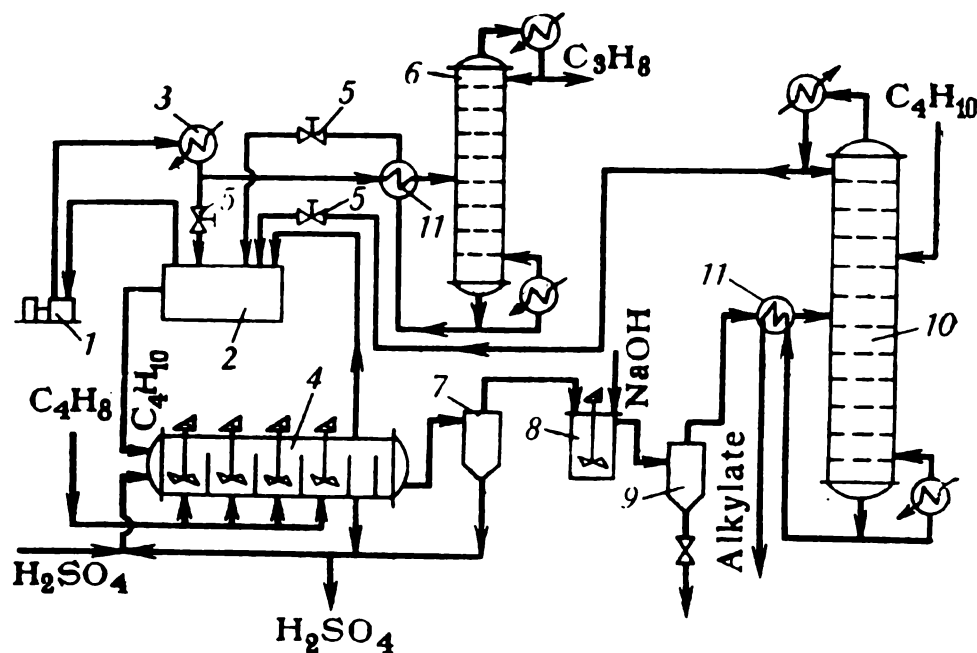


Fig. 4.5. Flow diagram of alkylation of isobutane by *n*-butylene:

1—compressor; 2—tank; 3—condenser; 4—reactor; 5—throttle valves; 6—depropanizer; 7, 9—separators; 8—neutralization unit; 10—debutanizer; 11—heat exchangers.

serves as a separator, where the acid is separated from the hydrocarbons and is returned to alkylation. The hydrocarbon mixture to be sent for further processing overflows through the last partition.

The flow diagram of the alkylation of isobutane by *n*-butylene is given in Fig. 4.5. Liquid isobutane, and recycle and fresh sulphuric acid are introduced into alkylator 4 (the first section from the left); liquid *n*-butylene is run into each of the sections. Part of the excess isobutane is evaporated by the heat evolved; its vapours pass into tank 2, which serves simultaneously as a receiver and a separator. The gas from this tank is continually run to compressor 1, where it is compressed up to 0.6 MPa and condensed under this pressure in water cooler 3. In throttle valve 5 the pressure is reduced to the operating pressure (≈ 0.2 MPa), part of isobutane being evaporated upon throttling and separated in tank 2. The liquid isobutane is then run into the alkylator, thus completing the cooling cycle. In the continuous operation, the propane formed as a result of the decomposition of the hydrocarbons plus the propane contained in a small amount in the starting hydrocarbon fractions is accumulated

in the isobutane. Therefore, a depropanizer—fractionating column 6—is included in the isobutane cooling cycle. Part of the recirculating isobutane is led from cooler 3 into column 6, and the isobutane purified from propane is returned after throttling into tank 2.

The mixture leaving the last section of alkylator 4 contains excess isobutane, octanes, *n*-butylene and other hydrocarbons (C_5 - C_7 and higher). It is run into separator 7 where it is separated from residual sulphuric acid. The acid is returned to the alkylator, but part of it is withdrawn from the system and fresh sulphuric acid is introduced instead. The hydrocarbon layer from separator 7 is neutralized with a 10-percent solution of caustic in apparatus 8 and the resulting emulsion is separated in separator 9. The neutralized hydrocarbon mixture is run into fractionating column 10 for the distillation of excess isobutane. For the isobutane to be condensed by a cheap cooling agent, water, a pressure of ≈ 0.6 MPa is maintained in the column. A fresh isobutane fraction is also introduced into this column. Part of the isobutane is returned to reflux column 10, the remainder being throttled and led to tank 2 and then recycled to reaction. This is the cycle of circulation of the isobutane. The commercial alkylate is withdrawn from the still of column 10.

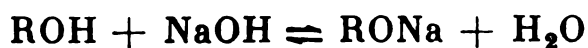
4.3. Alkylation at Oxygen, Sulphur and Nitrogen Atoms

The alkylation at O, S and N atoms is the principal method of synthesis of compounds with an ether linkage, mercaptans and amines.

4.3.1. O-Alkylation

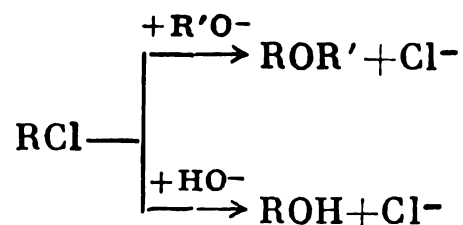
The O-alkylation processes that have become industrially important are (1) the alkylation of alcohols and phenols by chloro derivatives and (2) the alkylation of alcohols by olefins.

O-Alkylation by Chloro Derivatives. The reaction of chloro derivatives with alcohols is a reversible and very slow process, which is why it is carried out in the presence of alkalis, which convert alcohols or phenols into more reactive alcoholates (alkoxides) or phenolates (phenates):



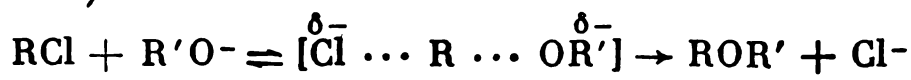
The equilibrium of the reaction is shifted to the right, the shift being the stronger the higher the acidity of the hydroxy derivative (phenols $>$ glycols $>$ monohydric alcohols) and the lower the concentration of water in the mixture. Since the presence of hydroxyl ions leads to the development of the side process of hydrolysis of

the chloro derivative



it follows that in order to raise the selectivity it is necessary to effect the reaction in an excess of the starting hydroxy compound with respect to the alkali and to limit the amount of water in order to shift the equilibrium of the protolytic exchange to the right. Even with more acidic phenol, which gives a phenolate with alkali in a nearly theoretical yield, the presence of free phenol in the mixture substantially increases the yield of the major product.

As far as the mechanism is concerned this process is analogous to the alkaline hydrolysis of chloro derivatives and belongs to the class of nucleophilic substitutions, which are second-order reactions (page 181):



It may also be accompanied by a parallel reaction of dehydrochlorination if the structure of the chloro derivatives permits.

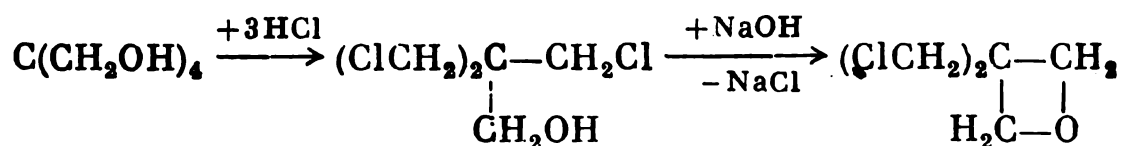
The synthesis of ethers from chloro derivatives is possible for a wide range of compounds, the reaction rate being dependent both on the nucleophilicity of the alcoholate (phenolate) and on the reactivity of the chloro derivative, which varies in a sequence typical of nucleophilic reactions.

The O-alkylation process is employed industrially on a small scale for the production of ethyl cellulose and benzyl cellulose from the corresponding chloro derivatives and cellulose, which are preliminarily treated with aqueous alkali. A product of the same type is *carboxymethyl cellulose*, which is made by heating alkali cellulose with sodium chloroacetate:

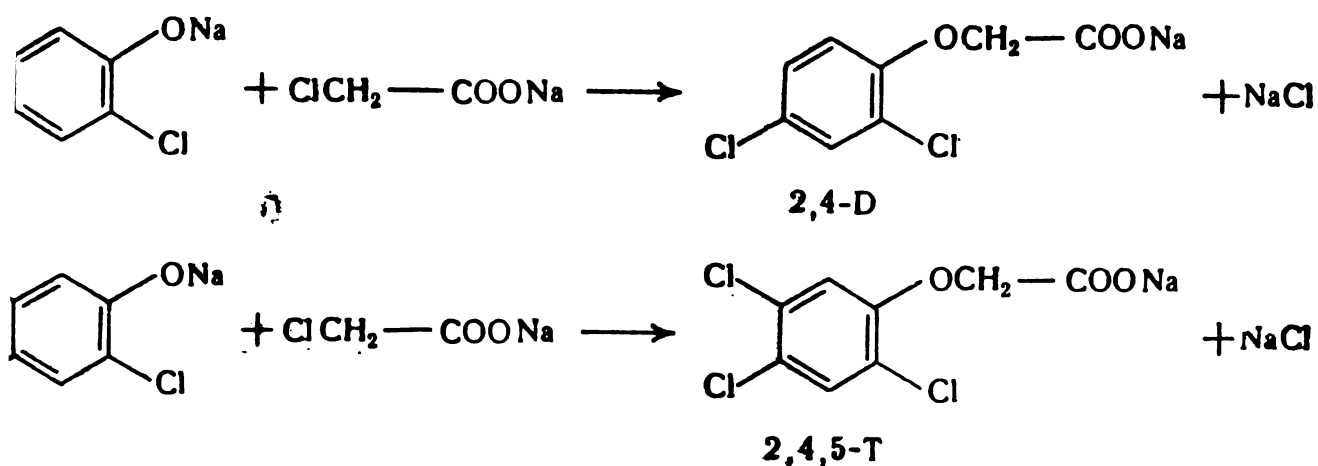


Carboxymethyl cellulose is capable of strongly increasing the viscosity of aqueous solutions, latexes and oils. It is an indispensable component of detergents and prevents the redeposition of dirt on the fabric.

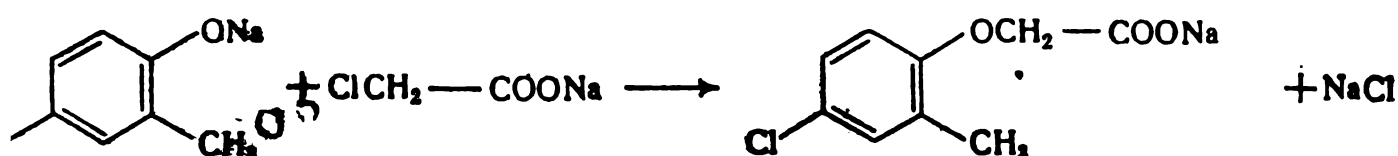
The O-alkylation reactions form the basis of the methods of synthesis of unsymmetrical ethers and some cyclic compounds, say the monomer bis(chloromethyl)oxacyclobutane:



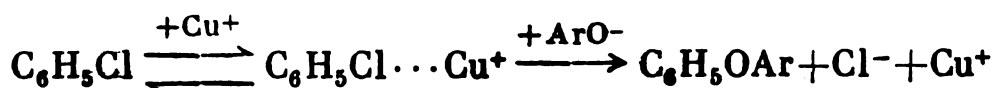
O-Alkylation is used for the synthesis of an important class of compounds with an ethereal linkage—salts of chlorophenoxyacetic acids, which are valuable herbicides. These compounds are all made by the interaction of the corresponding phenates with sodium mono-chloroacetate in aqueous solution. The most important of these are *4-dichlorophenoxyacetic acid* (2,4-D) and *2,4,5-trichlorophenoxyacetic acid* (2,4,5-T):



Another compound used for the same purpose is *2-methyl-4-chlorophenoxyacetic acid* made from 4-chloro-*o*-cresol and sodium monochloroacetate:



Analogous reactions with less reactive chlorobenzene (*arylation*) proceed under relatively mild conditions (200-250 °C) only when catalyzed by copper or its salts, which preliminarily activate the chlorine atom:

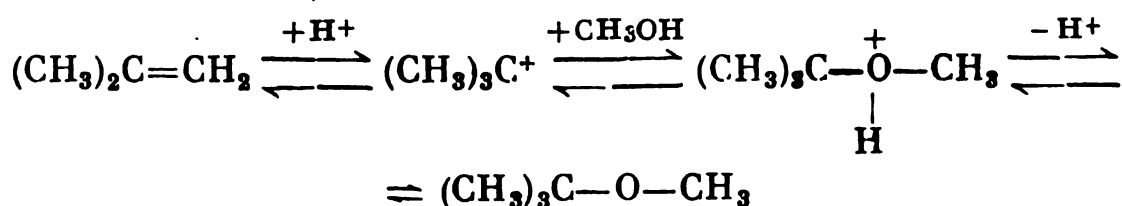


This route is used to produce diphenyl ether, $(\text{C}_6\text{H}_5)_2\text{O}$, and also polyphenyl ethers, $\text{C}_6\text{H}_5-(\text{OC}_6\text{H}_4)_n-\text{H}$, which are thermally stable heat carriers, lubricants, etc.

Technologically, these processes are similar in many respects to the hydrolysis of chloro derivatives involving the replacement of chlorine atoms (page 189). With water-insoluble chloro derivatives, the reaction mass consists of different phases, which is why its emulsification by way of agitation is important. In the production of salts of phenoxyacetic acids there takes place a homogeneous process, since all the reagents are soluble in water. Depending on the reactivity of the chloro derivative, the synthesis is accomplished in the temperature range of 60-200 °C and in order to keep the reaction mass in the liquid state, an elevated pressure is sometimes

required. In the batch operation, the process is carried out in an ordinary autoclave with a stirrer and a jacket for heating and cooling.

O-Alkylation by Olefins. The process has lately become commercially important for the synthesis of *tert*-butylmethyl ether, a high octane component of motor fuels. It is made from methanol and isobutylene in a reaction catalyzed by an acid catalyst:



The reaction proceeds with the evolution of heat and its equilibrium is displaced to the right with increasing pressure and decreasing

temperature. The most effective catalysts are cation-exchange resins at $\approx 100^\circ\text{C}$. Butylene fractions freed only from butadiene may be used as the feedstock since under the conditions indicated *n*-butylenes are incapable of reacting with methanol.

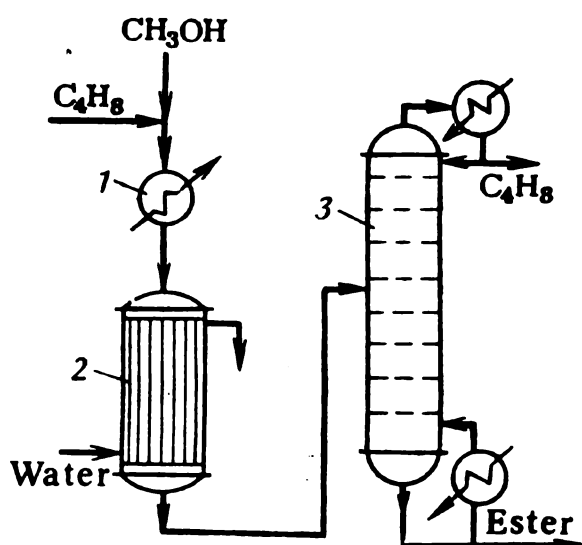


Fig. 4.6. Flow diagram for production of *tert*-butylmethyl ether:

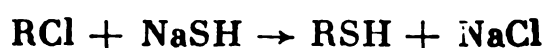
1—heater; 2—reactor; 3—fractionating column.

A simplified flow diagram of this process, which is employed in a number of countries, is shown in Fig. 4.6. Methanol and the butylene fraction are mixed under an appropriate pressure, heated and introduced into tubular reactor 2. The cation-exchange resin is in the tubes and the heat evolved is removed by water. The reaction

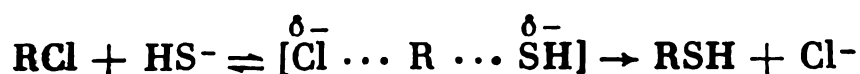
products are run to fractionating column 3, where the unconverted butylenes are distilled off, the *tert*-butylmethyl ether being left in the still. Another type of reactor, which has already been described in connection with the hydration of propylene with cation-exchange resins (see Fig. 3.9) may also be used for the synthesis; the temperature is controlled by introducing the cold feedstock separately into the sections of the reactor.

4.3.2. S-Alkylation

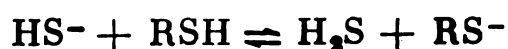
S-Alkylation by Chloro Derivatives. The reaction of chloro derivatives with sodium hydrosulphide, NaSH, yields mercaptans:



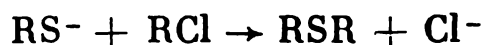
The reaction is irreversible and very closely resembles the alkaline hydrolysis of chloro derivatives. The only difference is that the HS^- ion, being a weak base, is an active nucleophile, which does not cause side dehydrochlorination reactions. Mechanistically, the reaction is a bimolecular nucleophilic substitution:



The resultant mercaptans are known to exhibit weak acidic properties as compared with hydrogen sulphide. Because of these properties they enter into an exchange reaction with the hydrosulphide:



The reaction of the RS^- ion with chloro derivatives gives dialkyl sulphide, which is the major by-product (just as is the case with the formation of ethers upon alkaline hydrolysis of chloro derivatives):



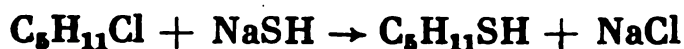
In order to reduce the formation of by-product dialkyl sulphide, the process must be carried out in an excess of sodium hydrosulphide based on the chloro derivative (in practice, use is made of a two-fold excess of the hydrosulphide). For the reaction mass to be homogenized, the process is conducted in a medium of methyl or ethyl alcohol or in aqueous-alcoholic solutions, in which the two reagents are soluble. The reaction temperature is 60–160°C, which sometimes requires the use of an increased pressure to keep the reaction mass in the liquid state. The process is operated batchwise in an autoclave equipped with a stirrer. In some isolated cases, it is carried out with an aqueous solution of NaSH in a two-phase medium.

Ethyl mercaptan, $\text{C}_2\text{H}_5\text{SH}$, commonly known as mercaptan, is made from ethyl chloride



and is used for the synthesis of one of the well-known insecticides—mercaptophos.

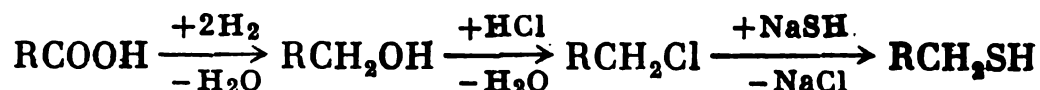
Ethyl mercaptan and *amyl mercaptan* obtained from chloropentanes



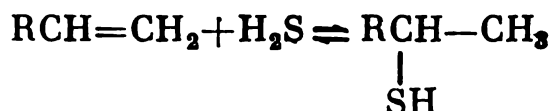
are used as LPG odorants.

The higher primary mercaptans (C_{10} – C_{15}) are of interest as intermediates in the synthesis of nonionic detergents based on ethylene oxide. They also find application as polymerization modifiers in the production of synthetic rubbers. They are produced by using as the feedstock the primary alcohols obtained by the hydrogenation of the corresponding carboxylic acids or by other methods. The

alcohol is converted to a chloro derivative and then to a mercaptan



Synthesis of Mercaptans from Olefins and Hydrogen Sulphide. The reaction of olefins with hydrogen sulphide is similar to the direct hydration of olefins and is also reversible:



However, its equilibrium is shifted to the right more strongly, and hydrogen sulphide is much more reactive than water, which allows the conditions of mercaptan synthesis to be varied over wide limits.

There are two methods for carrying out this process—a catalytic and a radical-chain method. In the first, use is made of various acid catalysts (protic acids, aluminosilicate, aluminium oxide, etc.). For instance, with aluminium oxide on silica gel the process is effected at 100–150 °C and ≈ 7 MPa in the liquid phase. The parameters depend on the reactivity of olefins, which increases in the following usual order: isoolefins $>$ n -olefins $>$ ethylene. The addition occurs according to the Markovnikov rule, which is why isoolefins give *tert*-alkylmercaptans:



Mercaptans are in turn capable of adding on across the double bond of the olefin, which gives rise to a system of consecutive-parallel reactions (compare with the formation of ethers upon hydration of olefins; page 197) leading to sulphides:



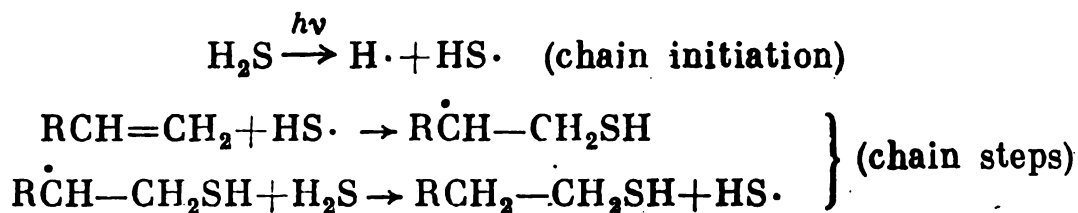
The formation of sulphides is undesirable, which is why the synthesis of mercaptans is carried out in an excess of hydrogen sulphide based on the olefin (the molar ratio is 1.5 : 1). In this way there are produced *tert*-alkylmercaptans from isobutylene or low-molecular-mass polymers of propylene or isobutylene (propylene tetramer, triisobutylene, etc.). Of prime industrial significance is *isododecyl mercaptan* (DDM), $\text{C}_{12}\text{H}_{25}\text{SH}$, which is used as a regulator of low-temperature polymerization in the synthesis of rubber.

The radical-chain addition of hydrogen sulphide to olefins occurs in the liquid phase at an ordinary or lowered temperature and upon irradiation with ultraviolet light. In this process, H_2S adds on contrary to Markovnikov's rule, this being typical of free-radical reactions. For instance, propylene gives *n*-propyl mercaptan and di-*n*-propyl sulphide:



The yield of the products is ≈ 90 percent with the reaction time being 5 min.

It is presumed that the mechanism of the radical-chain addition of hydrogen sulphide to olefins is as follows:

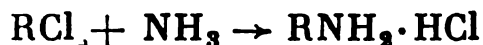


4.3.3. Synthesis of Amines by N-Alkylation Reactions

For ammonia and amines to be alkylated at the nitrogen atom, use is most often made of chloro derivatives and alcohols as alkylating agents. In contrast to many alkylation reactions, the use of olefins for this purpose leads only to the formation of a small amount of amines, nitriles being the major products.

4.3.3.1. Synthesis of Amines from Chloro Derivatives

The reactions of chloro derivatives with ammonia and amines in the gaseous state (neglecting the interaction of hydrogen chloride with these reagents) proceed with a very insignificant heat effect (see Table 4.1); thermodynamic calculations show that these reactions are reversible. Indeed, owing to the formation of a salt

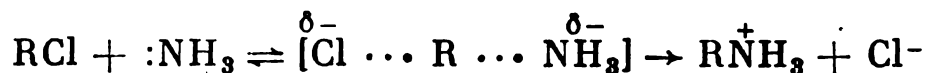


the reaction in the liquid phase becomes practically irreversible and its heat effect is $-\Delta H_{298}^\circ = (84-105) \text{ kJ/mol}$ (20-25 kcal/mol).

Aliphatic chloro derivatives react with ammonia and amines in the absence of catalysts, the reaction velocity being usually described by a second-order equation:

$$r = k[\text{RCl}][\text{NH}_3]$$

Mechanistically, it belongs to typical nucleophilic substitutions which proceed by way of the synchronous rupture of the old bond and formation of a new bond:

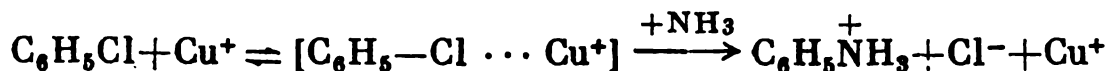


The reactivity of ammonia and amines varies in the following order:



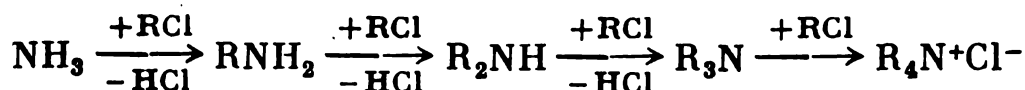
According to some data, primary aliphatic amines react with chloro derivatives at a rate 10 times faster than ammonia, and the latter reacts two times faster than aniline, but this depends on the temperature and the structure of the chloro derivative.

The reactivity of chloro derivatives in an interaction with ammonia or amines varies in the usual order: $\text{ArCH}_2\text{Cl} > \text{AlkCl} > \text{ArCl}$. As a result, for the reaction with chlorobenzene to be carried out successfully at a moderate temperature, catalysts are required. Cuprous salts, Cu_2Cl_2 , in the form of ammoniacal complexes have been found to be the best catalysts. Their catalytic action is accounted for by the formation of complex compounds with chlorobenzene, in which the C—Cl bond is significantly weakened and its rupture is facilitated by the action of ammonia:

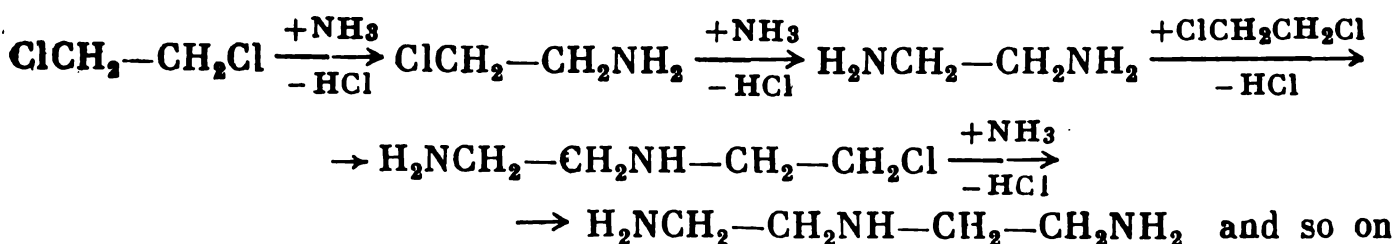


The interaction of chloro derivatives with ammonia and amines is commonly carried out in aqueous solutions, which give an alkaline reaction, which leads to the side hydrolysis of chloro derivatives with the formation of alcohols or phenols. In order to reduce the extent of the parallel hydrolysis reaction and, hence, to increase the yield of amines, it is necessary to use concentrated aqueous solutions of ammonia (25-30 percent), but even here about 5 percent of hydroxyl compounds is produced.

A very important feature of the N-alkylation of ammonia and amines by chloro derivatives is the consecutive-parallel course of the process, which results from the fact that the amine formed first can in turn react with the chloro derivative. This leads to the successive formation of a primary, a secondary and a tertiary amine; the tertiary amine when treated further with the chloro derivatives gives a tetrasubstituted ammonium salt:



With dichloro derivatives (say, 1,2-dichloroethane) both chlorine atoms are replaced, this resulting in a gradual lengthening of the chain due to the bifunctional nature of the reagents:



Just as with other irreversible consecutive-parallel reactions, the composition of the products depends on the ratio of the reagents. In this respect, there is a substantial difference between reactions of ammonia with aliphatic chloro derivatives and those of ammonia with aromatic chloro derivatives. For the former, the initial step proceeds at a much slower rate than the other steps, since an aliphatic amine is more reactive than ammonia and this is unfavourable

for the production of a primary amine. Its content in the reaction mass is low (Fig. 4.7a), and for its predominant formation (without considerable impurities of a secondary and a tertiary amine) a large excess of ammonia is required. In the industrial synthesis of primary amines the molar ratio of ammonia to the chloro derivative is kept within the limits of 10 : 1 to 30 : 1. In the reaction of ammonia with aromatic chloro derivatives the first step occurs faster than the second, which is much more favourable for the formation

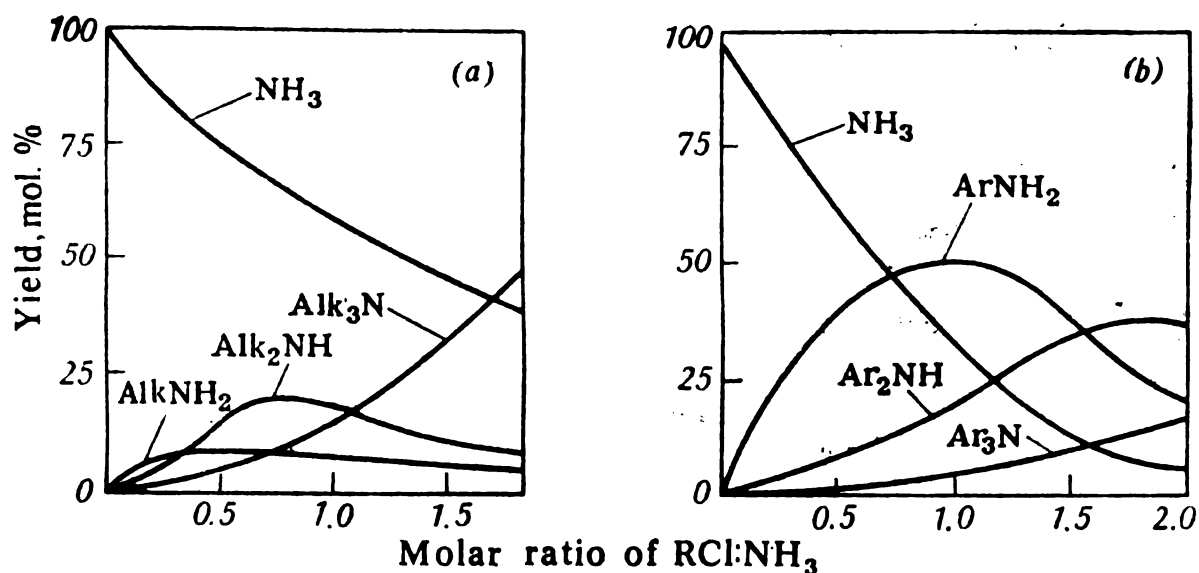


Fig. 4.7. Dependence of the composition of the reaction mass on the ratio of the reagents for the alkylation of ammonia by an aliphatic chloro derivative (a) and by chlorobenzene (b).

of a primary amine. The reaction mass contains a considerable quantity of a primary amine (Fig. 4.7b); for a primary amine to be produced with a small amount of a secondary amine present as an impurity, a relatively small excess of ammonia is sufficient. For example, in the production of aniline from chlorobenzene the molar ratio of ammonia to chlorobenzene is only 5 : 1.

The system of consecutive-parallel reactions in the synthesis of amines from chloro derivatives has one unusual feature. The hydrogen chloride formed combines with ammonia and amines into salts which are incapable of interacting with the chloro derivative. Evidently, the distribution of hydrogen chloride depends on the basicity of ammonia and amines, the following equilibrium being set up:

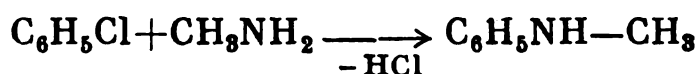


The high basicity of aliphatic amines is responsible for the shifting of the equilibrium to the right, but the excess of ammonia prevents this. As a result, a considerable proportion of the amine is nevertheless rendered unreactive and does not take part in the formation of the other products. This increases the yield of the primary amine, and the ammonium chloride added to the reaction mass enhances this effect even more. The same effect is exerted by carbon

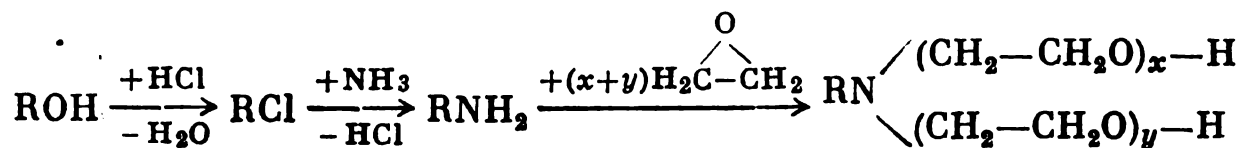
dioxide which binds the amines in the form of carbonates. When the synthesis is carried out in the presence of ammonium chloride or carbonate, a good yield of the primary amine is achieved even with a 2- to 4-fold excess of ammonia on the chloro derivative. In the synthesis of aromatic amines, which are weaker bases than ammonia, the same factors will obviously act in the reverse direction.

Products. When amines are produced from chloro derivatives, the chlorine is lost irreversibly and salt wastes are formed. This process is nevertheless employed for the synthesis of amines that cannot be obtained by other routes.

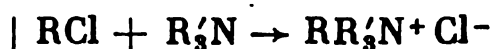
For example, from 1,2-dichloroethane and ammonia there is produced *ethylene diamine*, $\text{H}_2\text{NCH}_2\text{—CH}_2\text{NH}_2$, which is used as a corrosion inhibitor and for the manufacture of ethylenediamine-tetraacetic acid. Many other amines are also corrosion inhibitors. The synthesis of aniline from chlorobenzene and ammonia has proved to be economically unprofitable, but the production of monomethylaniline by this route is of some interest, since it is not accompanied by the formation of by-products that are inevitably formed during the alkylation of aniline:



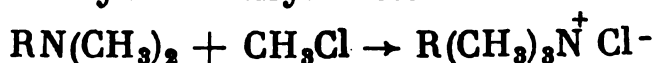
The higher primary amines obtainable from primary alcohols via the intermediate step of chloro derivatives are used in the production of nonionic surfactants:



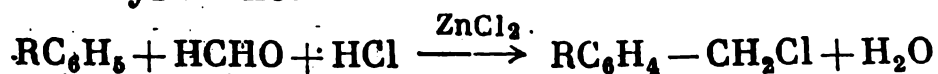
Cationic substances (in which the cation possesses surface-active properties) are typically quaternary ammonium salts. One of the routes to their synthesis is the interaction of tertiary amines (trimethylamine and triethylamine) and higher alkyl chlorides or alkylsulphuric acids:



The same reaction occurs between a tertiary amine with one long alkyl group and methyl or ethyl chloride:

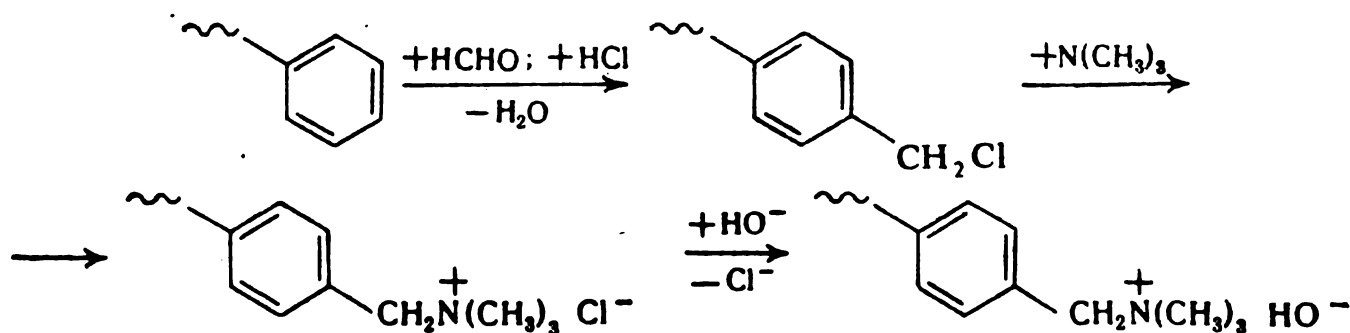


Isododecylbenzene or similar alkylbenzenes, including those obtained from α -olefins, are converted into cationic compounds by way of chloromethylation followed by an interaction with trimethylamine or triethylamine:



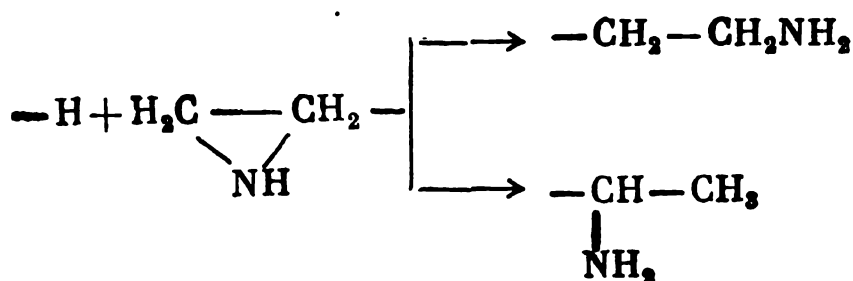
Cationic compounds are corrosion inhibitors and possess bactericidal, fungicidal and preserving properties, but they themselves have no detergent effect. They are used in the food and drug industries, usually in the form of mixtures with other detergents and small amounts of salts added.

N-Alkylation is also employed to produce one of the types of ion-exchange resins—*anion-exchange resins* containing the quaternary ammonium cation. For this purpose, for example, a structured copolymer of styrene and butadiene or divinyl benzene is chloromethylated and then treated with a tertiary amine:

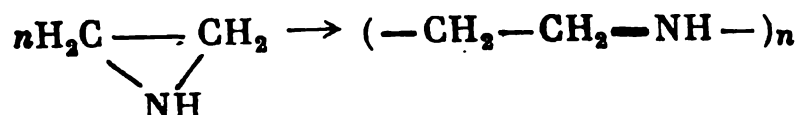


Anion-exchange resins are used to extract valuable metals contained in the form of complex anions, for the purification of solutions and also as basic catalysts.

A new interesting product of organic synthesis is *ethyleneimine* (a very toxic liquid; b.p. 56 °C). Owing to the presence of a reactive (highly strained) three-membered ring ethyleneimine reacts with the diverse compounds that contain mobile hydrogen atoms (*aminoethylation*):



and is polymerized with the formation of polyethyleneimines:

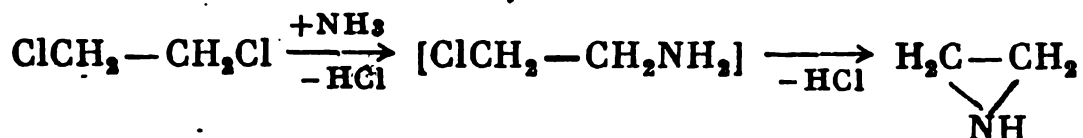


Ethyleneimine is obtained from monoethanolamine by way of an intramolecular N-alkylation with the closure of the three-membered ring. In one of the methods monoethanolamine is first converted at 160 °C to β -chloroethylamine, which is then treated at 90-95 °C with aqueous alkali to bind the hydrogen chloride evolved:



The ethyleneimine is distilled out of the reaction mass as it is formed.

The ethyleneimine ring is closed in one step by the action of ammonia on 1,2-dichloroethane in the presence of calcium oxide which binds hydrogen chloride:



This method is the simplest one and has found application on an industrial scale.

The homologues of ethyleneimine synthesized by analogous methods have also become of industrial value.

Technology of Synthesis of Amines from Chloro Derivatives. The reaction of chloro derivatives with ammonia and amines can be carried out both in the liquid phase, using aqueous solutions of ammonia, and in the vapour phase with anhydrous ammonia. The liquid-phase process is employed in the overwhelming majority of cases.

The temperature required to attain a sufficient reaction velocity depends strongly on the reactivity of the chloro derivative used. Usually the temperature range is 50-150 °C for aliphatic chloro derivatives and 200-240 °C for chlorobenzene. In order to maintain the reaction mass in the liquid state an elevated pressure is needed, the pressure being further increased due to the high pressure of vapours of ammonia over its aqueous concentrated solutions at these temperatures. The pressure used for different processes varies within the limits of 0.5-6 MPa. Most chloro derivatives do not dissolve in aqueous solutions of ammonia and the reaction proceeds in a two-phase medium. In this connection, of great importance for the intensification of the process is the emulsification of the reaction mass by way of stirring or vigorous agitation of the liquid. It is recommended that surfactants be used for the same purpose or the mixture be homogenized by using aqueous-alcoholic solutions of ammonia.

Batch processes of synthesis of amines from chloro derivatives are carried out in autoclaves equipped with a stirrer and a jacket for warming up the reaction mass by steam (or by high-temperature heat carriers) and for cooling with water. Continuous processes are effected in tubular reactors with small-diameter tubes, which make it possible to reduce the thickness of the walls and to create a fluidized flow of the liquid. One of the variants is to carry out the reaction in a system consisting of a preheater and an adiabatic reactor—in the first vessel the reaction mass is heated to the required temperature and is simultaneously emulsified. Because of the liberation of hydrogen chloride the material to be chosen for the reactor must be acid-resistant or it must be protected from corrosion.

However, for some aliphatic amines to be synthesized, use may be made of ordinary steel because amines inhibit acid corrosion.

When the reaction is completed, first the pressure is reduced. With the pressure being lowered the excess ammonia is vaporized and sent to the regeneration unit. The reaction liquid is cooled and neutralized by aqueous caustic (in the production of amines that are difficultly soluble in water it is better first to separate the layers and then to carry out a neutralization). Further processing of the neutralized mass after the excess ammonia is distilled off depends on the physical properties of the amine and is most often effected by way of extraction (or of steam distillation) and fractionation.

3.3.2. Synthesis of Amines from Alcohols

The reaction of alcohols with ammonia and amines



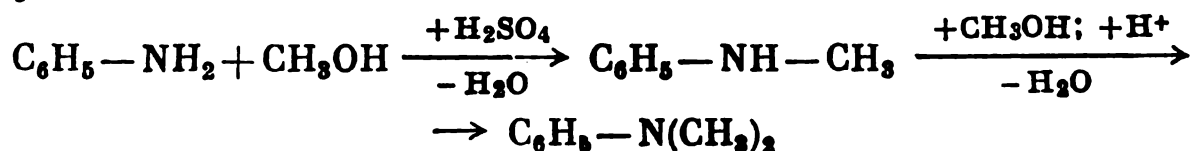
is an exothermic (see Table 4.1; page 255) and practically irreversible process. For example, for the reaction of methanol with ammonia the free energy change is expressed by the following equation:

$$\Delta G^\circ = -5600 + 0.9T$$

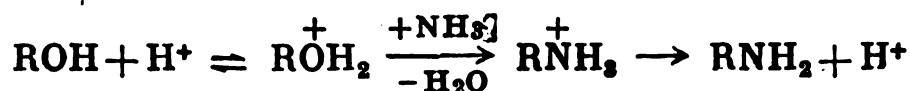
which gives a high value of the equilibrium constant at all permissible temperatures. By contrast, the interaction of phenols with ammonia and amines is reversible:



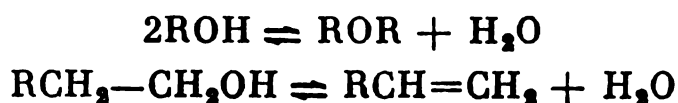
In the overwhelming majority of cases alcohols react with ammonia and amines only in the presence of catalysts. Methylanilines are produced from aniline and methanol by using sulphuric acid as catalyst:



But in reactions with higher alcohols there are formed a large number of by-products—ethers and olefins. The most popular catalysts used on an industrial scale are heterogeneous acid catalysts, in whose presence the process is conducted in the vapour phase at 50–450 °C. Use is most frequently made of aluminium oxide, aluminosilicates, aluminium phosphates, and ammonium phosphate. The action of heterogeneous catalysts consists of the activation of the C—O bond in an alcohol by way of chemisorption on their acid centres:

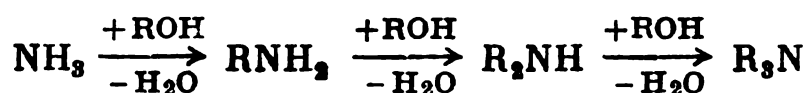


These catalysts are known to cause a dehydration of alcohols, leading to ethers and olefins:



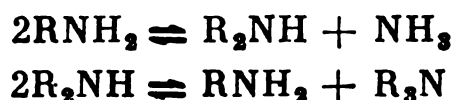
An ether is also capable of alkylating ammonia and amines, but the formation of an olefin is an undesirable side reaction. It can be suppressed to a considerable extent by using an excess of ammonia; in such cases the principal alkylation reaction is speeded up and the rate of dehydration is lowered. This route is successfully used to synthesize amines even from higher primary alcohols, which are even more strongly liable to undergo dehydration.

The reaction of ammonia with alcohols, like its interaction with chloro derivatives, is a consecutive-parallel process accompanied by the successive replacement of all the hydrogen atoms attached to nitrogen and by the formation of a mixture of primary, secondary and tertiary amines:



In this case too the ratio of the rate constants of the consecutive steps of the reaction is unfavourable for the production of a primary amine, since ammonia is a weaker base and a nucleophile. It has, however, been found that the same acid catalysts cause an intermolecular migration of alkyl groups which is analogous to that taking place in the transalkylation of aromatic compounds under the action of aluminium chloride.

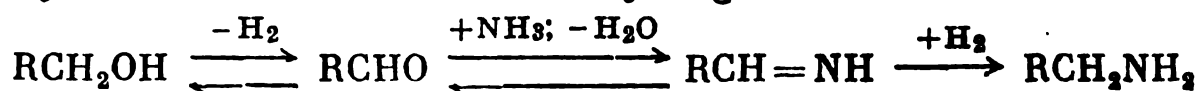
For example, methylamine undergoes disproportionation into a mixture containing about 33 percent NH_3 , 31 percent CH_3NH_2 , 32 percent $(\text{CH}_3)_2\text{NH}$ and 4 percent $(\text{CH}_3)_3\text{N}$; trimethylamine with ammonia also gives all the four products. Thus, there take place reversible reactions of transalkylation of amines



which have a strong impact on the composition of the alkylation products. Here, the equilibrium relationships are much more profitable than the kinetic ones for the production of a primary amine. Though in practice no complete equilibrium is attained, one may still use a relatively small excess of ammonia, which cuts down the cost of its regeneration. Moreover, if the major product of the process is, for example, a secondary amine, then it is possible to exclude the formation of a primary or a tertiary amines by recycling them to the reaction and to direct the process only in the desired direction. In such cases, in the reaction mass there are set up steady-state concentrations of the by-products corresponding to

the condition of equality of the rates of their formation and consumption.

The reaction between ammonia and alcohols can be carried out by using also dehydrogenation catalysts (copper, nickel, cobalt on an aluminium oxide support, for example). In this case, the reaction mechanism is quite different—first the alcohol is dehydrogenated to an aldehyde, this being followed by the condensation of the aldehyde with ammonia and the hydrogenation of the imine formed:



Process Technology. The alkylation of ammonia by alcohols is used on a large scale for the synthesis of lower aliphatic amines.

Methylamine, CH_3NH_2 (b.p. -6.8°C), *dimethylamine*, $(\text{CH}_3)_2\text{NH}$ (b.p. 7.4°C) and *trimethylamine*, $\text{N}(\text{CH}_3)_3$ (b.p. 3.5°C) are gases under ordinary conditions. *Ethylamine*, $\text{C}_2\text{H}_5\text{NH}_2$ (b.p. 16.5°C), *diethylamine*, $(\text{C}_2\text{H}_5)_2\text{NH}$ (b.p. 55.9°C) and *triethylamine*, $(\text{C}_2\text{H}_5)_3\text{N}$ (b.p. 89.5°C) are liquids. These compounds are all miscible with water in all proportions, form explosive mixtures with air and are highly toxic compounds, just as most of the other amines. Methylamines and ethylamines are commercially produced from alcohols and ammonia. They are used as fuels for liquid-propellant rocket engines and as intermediates in organic synthesis (the production of other amines, dimethyl hydrazine, anion-exchange resins and anionic compounds, pesticides of the simazine type and also carbamates and dithiocarbamates).

This route is also employed to obtain *propylamine*, *butylamine* and some higher homologues from the corresponding alcohols.

The synthesis of amines is carried out in the vapour phase at $380\text{--}450^\circ\text{C}$ and $2\text{--}5\text{ MPa}$. The pressure is used to raise the capacity of the plant, to reduce the size of the vessels used and to suppress the side dehydration of the alcohol. The catalyst used is active aluminium oxide or aluminosilicate; sometimes promoters are added to these catalysts. In such cases, the reaction is a typical heterogeneous-catalytic process, and its low heat effect makes it possible to use adiabatic reactors with a continuous fixed catalyst bed. The molar ratio of ammonia to alcohol (methyl or ethyl alcohol) is $\approx 4 : 1$; primary, secondary and tertiary amines can be produced in any ratio by recycling part of each of the amines (most often it is trimethylamine) to the reaction. The excess ammonia, unconverted alcohol and ether are also recirculated.

The flowsheet of the production of methylamines is given in Fig. 4.8. Fresh methanol, ammonia and recycle are mixed at $2\text{--}5\text{ MPa}$ in mixer 1 and led to heat exchanger 2, where they are vaporized and heated by hot reaction gases. The reactions described above take place in reactor 3, giving amines with a nearly complete conversion

of the methanol. The hot gases give off their heat to the starting mixture in heat exchanger 2 and are sent for further processing.

The products formed are separated by a multistep fractionation; at each step use is made of a pressure that can provide a reflux by way of cooling with water. First, in column 4 the most volatile ammonia is distilled off and recycled. The still liquid is run to column 5 for extractive distillation with water (in the presence of water the relative volatility of trimethylamine becomes the highest among other methylamines). The trimethylamine (TMA) distilled off may be partly removed as a commercial product, but the

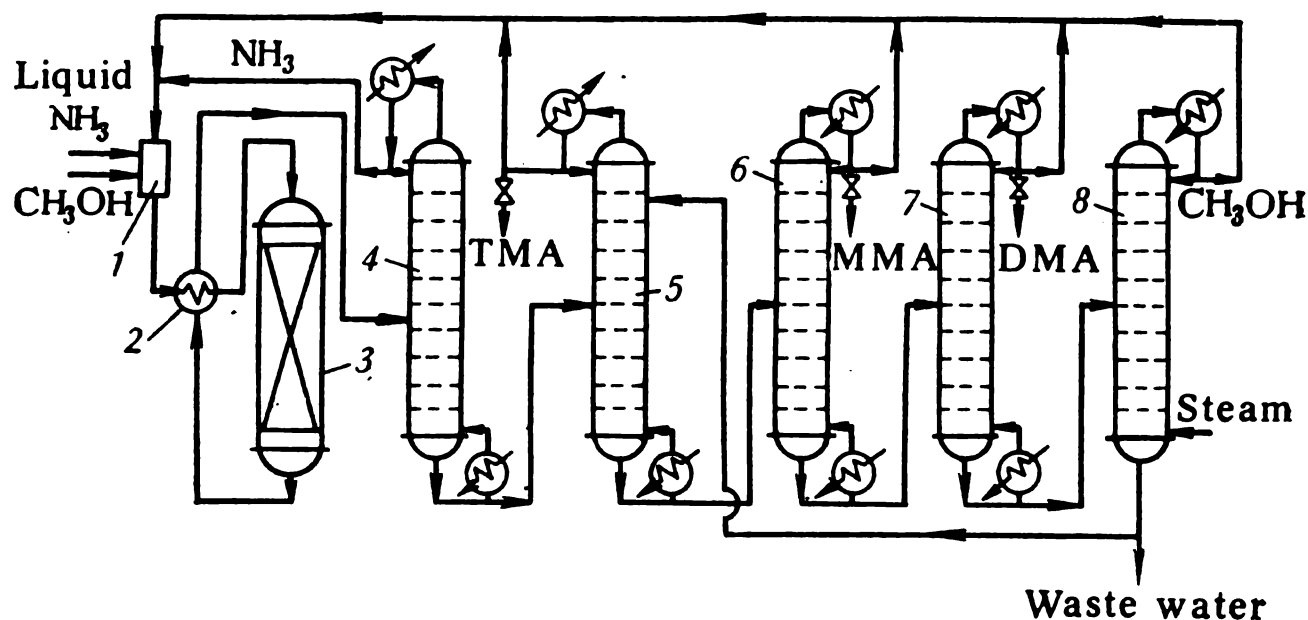


Fig. 4.8. Flow diagram for production of methylamines:

1—mixer; 2—heat exchanger; 3—reactor; 4, 5, 6, 7, 8—fractionating columns.

major proportion is recycled. The difference between the boiling points of the other two amines is stronger (-6.8 and 7.4°C), and they can be separated by ordinary fractionation in column 6 (monomethylamine, MMA) and column 7 (dimethylamine, DMA). Each of these can be taken overhead as commercial products or they are partly (or completely) recycled.

Finally, in column 8 the unconverted methanol is distilled off from the waste waters and returned to the reaction. The total yield of the amines with account taken of all the losses amounts to 95 per cent.

In the synthesis of ethylamines the preparation of the starting mixture and the reaction unit are analogous to those shown in Fig. 4.8. The separation of the amines is facilitated due to a large difference in boiling point (16.5 , 55.9 and 89.5°C) and is effected by ordinary fractionation, the order of distillation being as follows: ammonia, monoethylamine, diethylamine and triethylamine. The by-product is ethylene, which is withdrawn from the system upon condensation of the mixture before the ammonia is distilled off.

4. β -Ethoxylation and Other Syntheses Based on α -Oxides

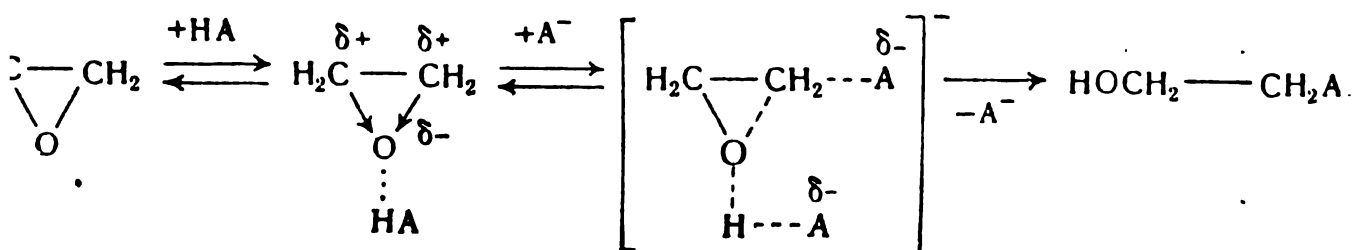
α -Oxides become increasingly important for the production of any valuable compounds, especially glycols, glycerine, ethanolamines, nonionic surfactants, high-molecular-mass compounds, etc.

4.1. Chemistry and Theoretical Foundations

Syntheses from α -Oxides

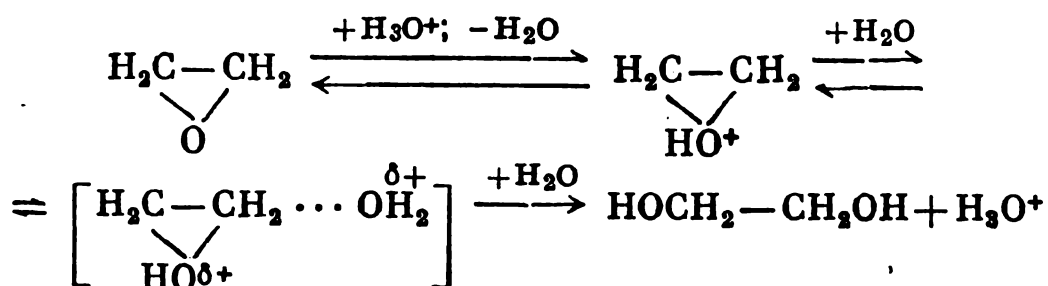
The most important group of reactions of α -oxides consists of the addition of compounds with sufficiently mobile (replaceable) hydrogen atoms (H_2O , ROH , ArOH , H_2S , HCN , RCOOH). These reactions can proceed in the absence of catalysts and upon acidic and basic (nucleophilic) catalysis. In the latter case, the catalyst is the conjugate base of the acid-reagent (i.e., HO^- , RO^- , ArO^- , HS^- , N^- , RCOO^-).

The mechanism of the reaction involves a preliminary activation of the α -oxide at its oxygen atom, which facilitates the subsequent attack of the nucleophile on the carbon atom, as a result of which the ring is opened:



The noncatalytic reaction proceeds by the same mechanism, the only difference being that the nucleophile is the molecule of the reagent itself. Since it is less active than the corresponding conjugate base, the noncatalytic reaction occurs much more slowly (a sufficient reaction velocity is attained at 150-200 °C; in nucleophilic catalysis it is achieved at 80-120 °C).

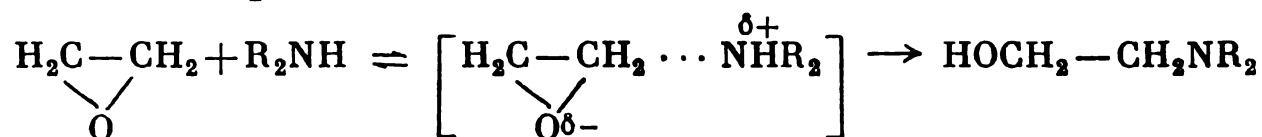
The acidic catalysis of the same reactions by protic acids is effective only in strongly polar media (water, lower alcohols) and occurs by the following mechanism:



In a weakly polar medium, protic acids readily add on to α -oxides and become inactive. In these conditions the catalysis by aprotic

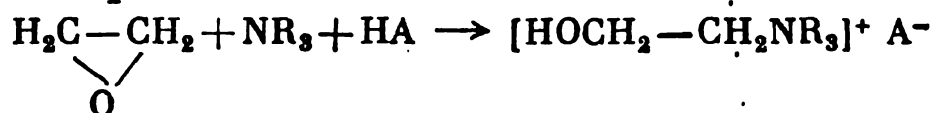
acids (BF_3 , SnCl_4) and sometimes by some heterogeneous acid catalysts (aluminium oxide treated with HF , etc.) is very effective. Its mechanism is analogous to that given above, the reactions catalyzed by acids proceed in temperature ranges of 20-40 to 100-150 °C.

Upon interaction with compounds which are themselves rather strong nucleophiles (NH_3 and amines) the ring can be opened without an electrophile:



However, if the mixture contains water or any other compound with mobile hydrogen atoms, these activate, as described above, the oxide ring and the reaction is substantially accelerated and proceeds at a sufficient velocity at 40-100 °C.

A number of reactions of α -oxides are effectively catalyzed by tertiary amines, which accounts for the formation of quaternary ammonium compounds:



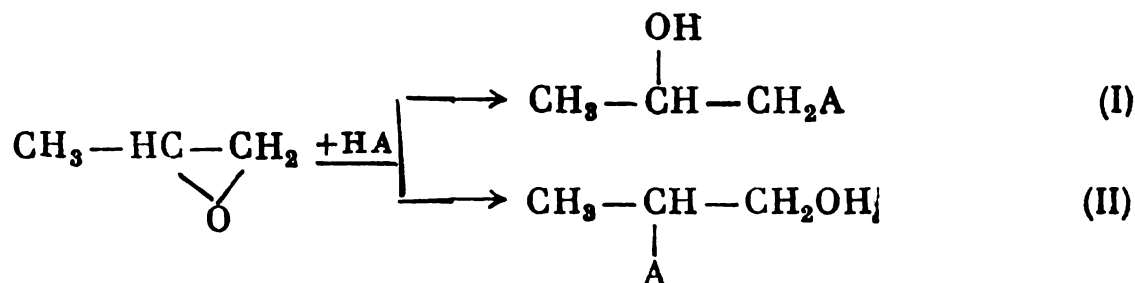
Since such compounds have a bulky cation and are better soluble, they prove to be active catalysts in weakly polar media than alkali-metal compounds.

In accordance with what has been said above, the rate of most reactions of α -oxides is proportional to the concentrations of the α -oxide, the proton-donor (H_3O^+ , HA , etc.) and of the nucleophile (A^- , HA , R_2NH , etc.). However, the resultant product, which also exhibits acidic properties, takes part in the activation of the ring too:

$$r = \{k_1[\text{AH}] + k_2[\text{ACH}_2-\text{CH}_2\text{OH}]\} \left[\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \end{array} \right] [\text{Nu}]$$

Not infrequently this leads to autocatalysis, which is especially noticeable in reactions with mercaptans and amines.

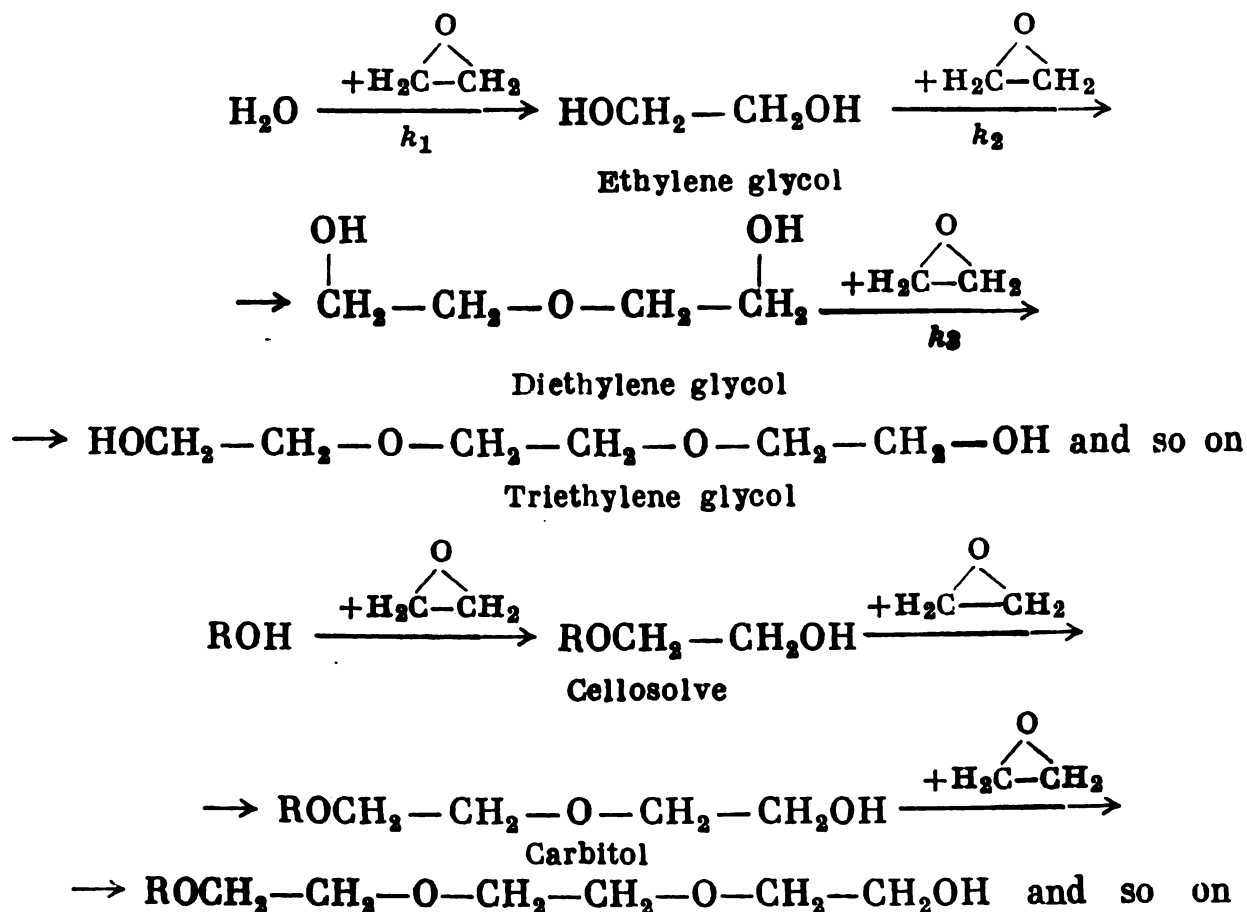
With unsymmetrical α -oxides the addition may proceed in two directions:



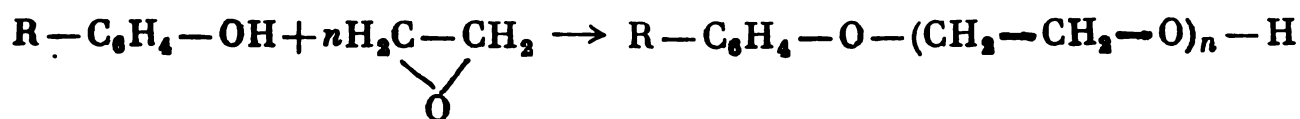
With electron-releasing substituents and with the oxide ring being weakly activated by acids (nucleophilic catalysis and the noncatalytic reaction with water, alcohols, etc.) the reactivity of

substituted oxides decreases and 95-99 percent of the product of "normal" substitution (I) is formed. Upon reaction with more acidic compounds and especially upon acidic catalysis the reactivity increases and a considerable quantity of the "anomalous" isomer (II) is formed, this being valid to a greater extent for α -oxides with electron-attracting substituents.

Products and Regularities of Successive Oxyethylation. In most of the reactions discussed above the products formed contain groupings capable of further addition of α -oxides. This causes the occurrence of consecutive-parallel reactions leading to the formation of products of increasing degree of oxyethylation (ethoxylation):



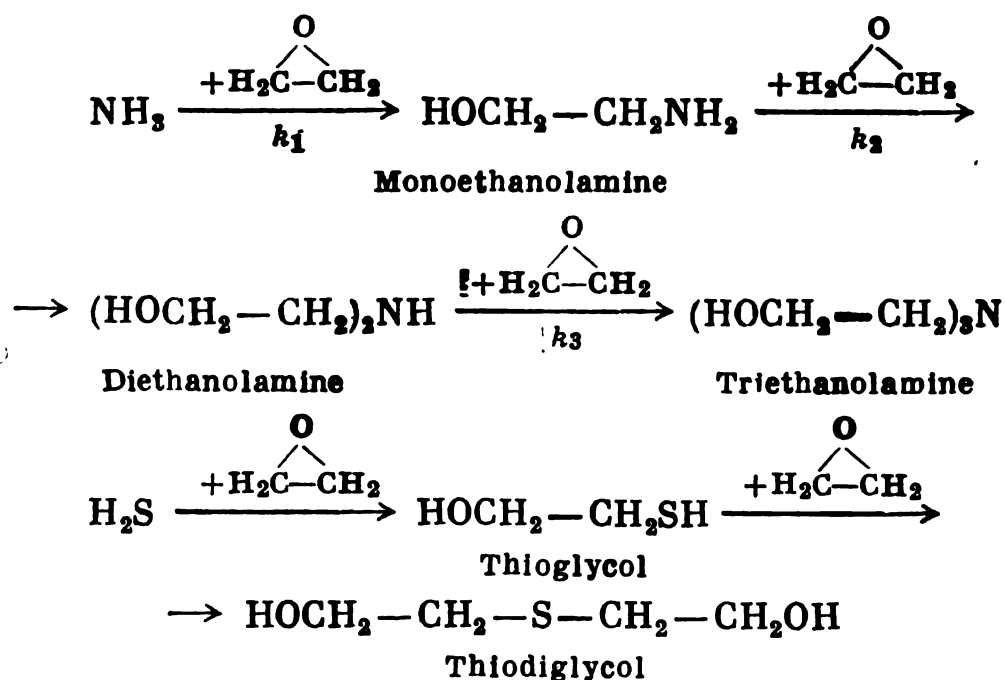
These processes are sometimes undesirable (for example, in the production of ethylene glycol or ethylcellosolve), but in other cases, on the contrary, they are employed for the manufacture of diethylene glycol, carbitols and nonionic surfactants containing a long chain of oxyethyl groups:



As the consecutive-parallel reactions are progressing there are formed high-molecular-mass polymers of α -oxides.

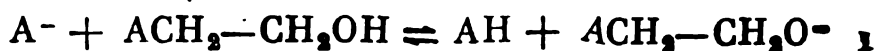
The interaction of α -oxides with ammonia, amines, amides, hydrogen sulphide is also accompanied by a successive addition of α -oxide molecules, but primarily due to the replacement of the hydrogen

atoms attached to nitrogen or sulphur:



The composition of the products formed and the selectivity of the process based on the end product depend on the ratio of the rate constants of the successive steps of the reaction and on the ratio of the reagents. The first of these factors is determined in turn by the properties of the reactants and products and also by the type of the reaction of α -oxides.

Upon nucleophilic catalysis the base enters into a protolytic exchange with the reaction products:



the state of equilibrium being dependent on the concentrations of the components of the mixture and their basicity. That is why a relatively large portion of the catalyst is in the form of the conjugate base of the more acidic component of the mixture, which contributes to an increased formation of the product of its addition to the α -oxide. Here, the differential selectivity with respect to the first intermediate product is described by the following equation:

$$\Phi_B = 1 - \frac{k_2}{k_1} \frac{[\text{ACH}_2-\text{CH}_2\text{OH}]}{[\text{AH}]} = 1 - \frac{G_2}{G_1} \left(\frac{K_2}{K_1} \right)^\alpha \frac{[\text{ACH}_2-\text{CH}_2\text{OH}]}{[\text{AH}]}$$

where K_2/K_1 is the ratio of the basicities of the first product and the reactant; G and α are the constants in the Brönsted equation. It has been found that the same equation holds for the noncatalytic reaction and acidic catalysis, but the value of α is different for different types of reactions: 0.65 for nucleophilic catalysis; 0.22 for noncatalytic reactions and 0.13 for acidic catalysis (Fig. 4.9).

On this basis one can predict the results and choose the optimal type of reaction of α -oxides for a particular process. For example, in the directed synthesis of the first products of the addition to re-

agents of considerable acidity (acids, phenols), when $K_1 \gg K_2$, nucleophilic catalysis is more favourable because it enables the selectivity to be increased substantially. At $K_1 \approx K_2$, the type of reaction has a slight effect on the selectivity, but here too the use of nucleophilic catalysis is preferred (reactions with glycols and oxyethylated compounds). But in reactions with reagents that are less acidic than the first addition product (reactions with water and primary and especially secondary alcohols) nucleophilic catalysis gives low selectivity, and it is obvious that at $K_2 > K_1$ best results can be obtained with non-catalytic reactions and especially with acidic catalysis. These conclusions do not apply to reactions with ammonia and amines, whose relative reactivity varies in the usual order ($\text{NH}_3 \ll \text{RNH}_2 \approx \text{R}_2\text{NH}$).

The regularities considered above govern the dependence of the composition of the reaction mass on the molar ratio of ethylene oxide to the reagent and the integral selectivity of the process.

In reactions of α -oxides with water, monohydric alcohols and ammonia the first addition step always proceeds more slowly than the second, but the subsequent steps occur with about the same velocity as the second. For example, in the system of reactions of ethylene oxide with water given above the ratio of the rate constants k_2/k_1 is 7 : 1, i.e., much greater than unity. As is known, in such consecutive-parallel processes the formation of the first intermediate is insignificant and its maximum is displaced to low molar ratios of ethylene oxide to the reagent. A plot of the composition of the products in such reactions against the ratio of the reagents is given in Fig. 4.10a.

Quite different regularities are observed in the interaction of α -oxides with compounds having stronger acidic properties (carboxylic acids, phenols, hydrocyanic acid, mercaptans) under the conditions of basic catalysis, which is commonly used for these reactions. Here the first addition step is distinctly separated from the subsequent steps, the first intermediate can be obtained in a yield close to 100 percent, and only after the reactant is used up completely can there be obtained the subsequent products of the addition of α -oxides (Fig. 4.10b).

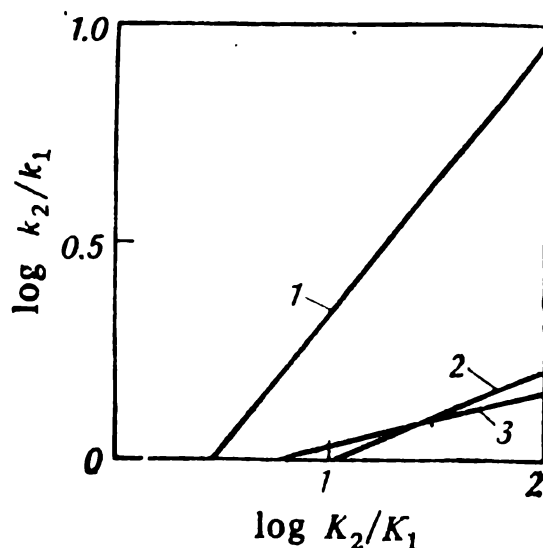


Fig. 4.9. The logarithmic dependence of the ratio of the rate constants of the sequential ethoxylation of alcohols on the ratio of the acidities of the β -oxysubstituted product and alcohol: 1—nucleophilic catalysis; 2—noncatalytic reaction; 3—acidic catalysis.

In order to attain a high yield of the final product in each particular case one must choose the optimal ratio of the reagents with account taken of the cost of the distillation and recirculation of the excess reagent. For example, in the production of ethylene glycol and propylene glycol or cellosolves (i.e., upon introduction

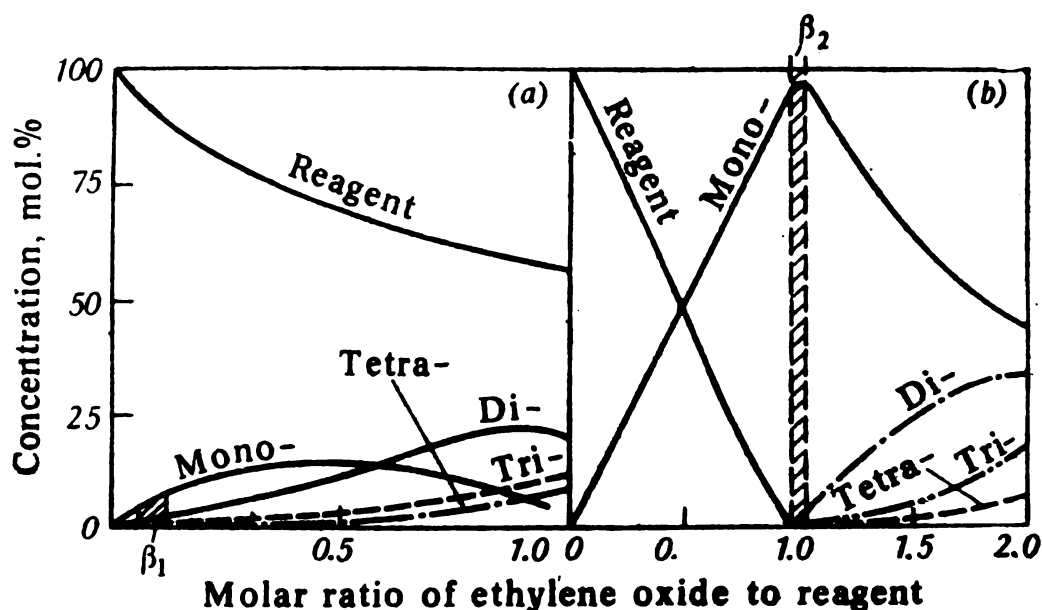


Fig. 4.10. Dependence of the composition of the products of ethoxylation on the ratio of the reagents:

(a) reaction with water or alcohol; (b) reactions with phenol or carboxylic acid.

of one oxyethyl group) the reaction is always carried out with a deficiency of ethylene oxide (the molar ratio ranges from 1 : 7 to 1 : 15 upwards; the quantity β_1 in Fig. 4.10a).

The molar ratio of the reagents in the production of monooxyethylated derivatives of carboxylic acids, phenols, mercaptans and other compounds exhibiting acidic properties may be close to unity (the quantity β_2 in Fig. 4.10b). Even a small excess of the unconverted acidic reagent provides the formation of a monooxyethylated derivative in a yield of about 100 percent. By contrast, in the synthesis of polyoxyethylated compounds (polyglycols, nonionic detergents) an excess of the α -oxide corresponding to the desired chain length is required.

4.4.2. Technology of Syntheses from α -Oxides

Of these processes, the syntheses from ethylene oxide are of prime industrial significance, those from propylene oxide being less important. It should be recalled that these compounds are volatile liquids (b.p. 10.6 and 33.9 °C, respectively), which are toxic and form highly flammable mixtures with air. Another industrially important epoxide, epichlorohydrin, and the production of glycerine from it have already been described (pages 188 and 192).

4.4.2.1. Products Obtained from α -Oxides

Glycols and Their Ethers. The largest quantity of α -oxides is consumed for the manufacture of glycols and their ethers.

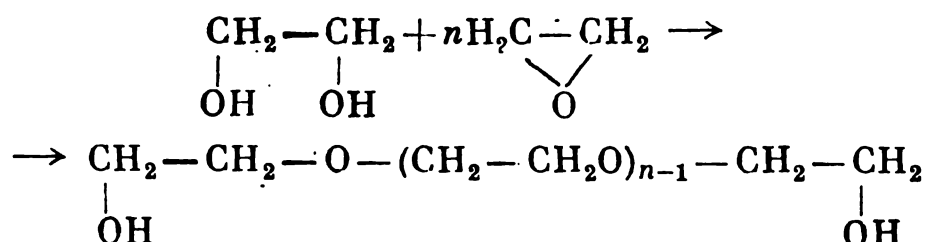
Ethylene glycol (glycol), $\text{HOCH}_2\text{—CH}_2\text{OH}$, is an oily, colourless liquid (b.p. 197°C), which is miscible with water in all proportions. Technically, it is used in large quantities for the production of antifreezes—mixtures with water which do not freeze at low temperatures and which are used for automotive cooling systems in winter conditions. Ethylene glycol is also used in the synthesis of polymeric materials—polyethylene terephthalate (lavan), unsaturated polyesters, polyurethanes, alkyd polymers, etc. It is also the feedstock for the production of ethylene glycol dinitrate (used for the manufacture of explosives and gun powders) and ethylene glycol monoacetate and diacetate, which are good solvents.

The most important industrial method of synthesis of ethylene glycol consists of the hydration of ethylene oxide usually carried out in the absence of catalysts at $170\text{--}200^\circ\text{C}$ and with a 15-fold excess of water. This synthesis is reported to have been accomplished under milder conditions in the presence of phosphoric acid as catalyst.

Diethylene glycol (diglycol), $\text{HOCH}_2\text{—CH}_2\text{—O—CH}_2\text{—CH}_2\text{OH}$, is a colourless water-miscible liquid (b.p. 245°C). Like ethylene glycol, it is used for the synthesis of polyesters. The esters of diethylene glycol with monocarboxylic acids ($\text{C}_7\text{--C}_{10}$) find uses as plasticizers and lubricating oils. Large quantities of diethylene glycol are used for the production of an explosive—diethylene glycol dinitrate. Diglycol is extensively employed in the oil-refining industry for dehydration of natural gas and extraction of aromatic hydrocarbons.

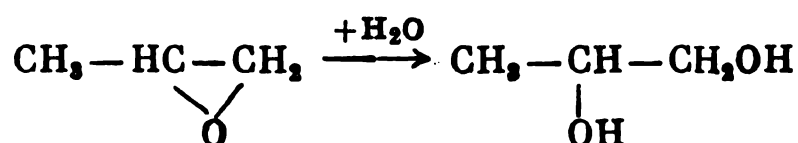
Diglycol is the second product of the oxyethylation of water (page 299) and is made with a smaller molar excess of water (from 4 : 1 to 5 : 1), the intermediate ethylene glycol being recycled to the reaction.

The by-products in the production of ethylene glycol and diethylene glycol are *triethylene glycol (triglycol)* and *polyglycols (polyoxyethylene esters)*. These compounds are sirupy water-miscible liquids. Triethylene glycol is used for the synthesis of some polyesters. Triglycol and polyethylene glycols in the form of their esters with carboxylic acids ($\text{C}_6\text{--C}_{10}$) find application as plasticizers and lubricating oils. Polyglycols are made by the oxyethylation of ethylene glycol in the presence of alkalis at $100\text{--}130^\circ\text{C}$:



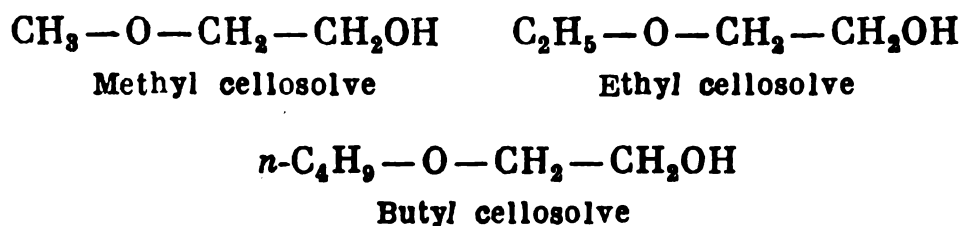
Polyglycols with a molecular mass lower than 600 are viscous liquids; those with a molecular mass ranging from 4000 to 6000 (high-molecular compounds) are waxy solids (Carbowax) having a low softening point (40-60 °C). Polyglycols are used as lubricants, high-temperature heat-exchange media, softeners and foam-quenching agents.

Propylene glycol, $\text{CH}_3\text{—CH(OH)—CH}_2\text{OH}$, can replace ethylene glycol in many fields of application. It is made by the hydration of propylene oxide in a manner analogous to the hydration of ethylene oxide:



Dipropylene glycol and polypropylene glycols formed as by-products can be used for the preparation of polyesters, plasticizers and lubricating oils.

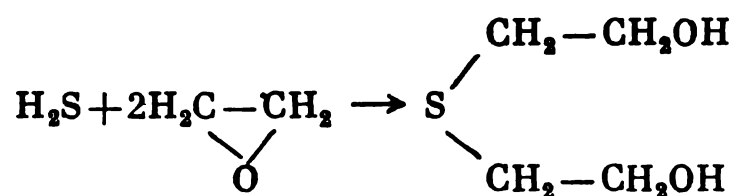
Cellosolves are the monoethers of ethylene glycol having the general formula $\text{ROCH}_2\text{—CH}_2\text{OH}$. These compounds owe their name to the fact that they are good solvents for cellulose ethers. The most frequently used solvent is *ethyl cellosolve*; *methyl cellosolve* and *butyl cellosolve* are used less frequently:



Butyl cellosolve and higher cellosolves are used in the form of their esters with dicarboxylic acids as plasticizers. All cellosolves are made by the interaction of ethylene oxide with the corresponding alcohols at $\approx 200^\circ\text{C}$ and with a molar alcohol/ α -oxide ratio of 7 : 1 to 8 : 1.

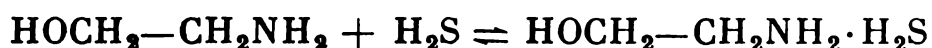
The by-products formed are carbitols—the monoethers of diethylene glycol. They are used as solvents and also for the synthesis of plasticizers.

Thioglycols. These compounds are obtained by the interaction of ethylene oxide with hydrogen sulphide and mercaptans at elevated temperature; the reaction proceeds even in the absence of a catalyst. With stoichiometric ratios hydrogen sulphide gives *thiodiglycol*



and monomethacrylate of ethylene glycol, which are valuable monomers, and also of ethylene glycol monoterephthalate, which can be directly converted into a polymer by polycondensation. The most effective catalysts used for reactions of α -oxides with carboxylic acids are tertiary amines, which function in the form of quaternary ammonium salts.

Ethanolamines. *Monoethanolamine*, $\text{H}_2\text{NCH}_2\text{—CH}_2\text{OH}$ (b.p. 172.2°C), *diethanolamine*, $\text{HN}(\text{CH}_2\text{—CH}_2\text{OH})_2$ (b.p. 268°C) and *triethanolamine*, $\text{N}(\text{CH}_2\text{—CH}_2\text{OH})_3$ (b.p. 360°C) are sirupy water-miscible liquids, which exhibit strong basic properties. Their chief outlets are in the purification of gases from acidic impurities (H_2S , CO_2). For this purpose, use is made of mixtures of ethanolamines to which water is added to lower their viscosity. At low temperature with acid impurities they form salts, which when heated decompose with the recovery of the ethanolamines:



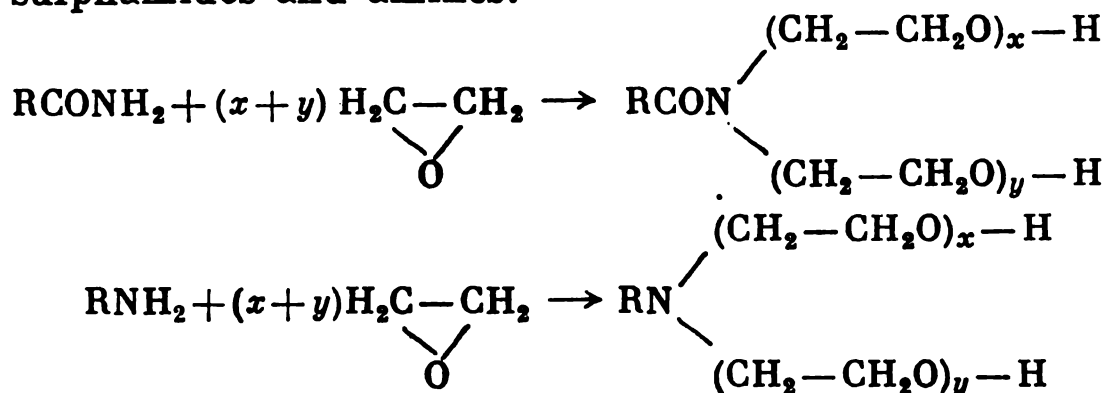
The salts of ethanolamines $\text{RCOO}^- \text{NH}^+(\text{CH}_2\text{—CH}_2\text{OH})_3$ and the ethanolamides of higher carboxylic acids, $\text{RCONH—CH}_2\text{CH}_2\text{OH}$, exhibit surface-active and foaming properties and can be used as components of detergents and humectants. Ethanolamines are also used as the feedstock for the synthesis of morpholine, ethyleneimine and some explosives.

Ethanolamines are made by reacting ethylene oxide with ammonia. The process is carried out with an aqueous solution of NH_3 at $40\text{--}60^\circ\text{C}$, which is associated with the necessity to distill off large amounts of water during the derivation of ethanolamines. Because of the basic properties of ammonia and ethanolamines and also of the formation of by-product quaternary ammonium hydroxide, which catalyzes the hydration of the α -oxide, ethylene glycol is formed as a by-product. The selectivity of the reaction can be enhanced by addition of CO_2 to the reaction mixture; carbon dioxide neutralizes the hydroxyl ions.

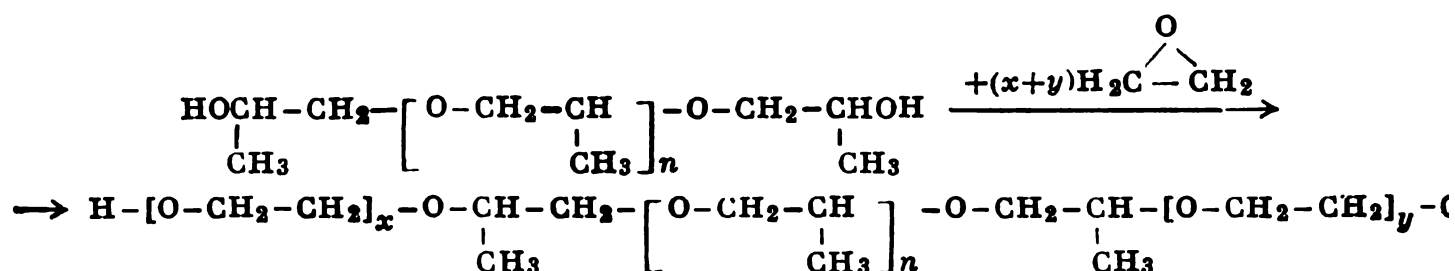
In the process that has been recently developed, ethanolamines are produced from ammonia and ethylene oxide with only a small amount of water added; water catalyzes the initial step of the reaction and eliminates the induction period. At $100\text{--}130^\circ\text{C}$ a pressure of $7\text{--}10\text{ MPa}$ is required in order to maintain the reaction mixture in the liquid state. With the molar ammonia-ethylene oxide ratio equal to $15 : 1$ there is obtained a mixture of 80 percent monoethanolamine, 16 percent diethanolamine and 4 percent triethanolamine; no by-product glycol is formed. The merits of the method are high efficiency and the considerably reduced cost of the distillation and recirculation of water.

Of considerable commercial interest are also *alkylethanolamines* and *arylethanolamines*, which are made by reacting ethylene oxide

4. The products of the polyoxyethylation of amides of higher acids, sulphamides and amines:



5. Polymeric nonionic detergents, in which the hydrophobic groupings are polypropylene glycols, whose molecular mass (ranging from 800 to several thousands) and methyl groups render them capable of exerting a rather strong hydrophobic action. The oxyethylation of such polypropylene glycols across the end hydroxyl groups leads to detergents:



These products are all water-soluble, viscous liquids, pastes or waxy solids. Their physical and technical properties can be varied over wide limits by choosing the hydrophobic portion of the molecule and the number of oxyethylene groups in the hydrophilic chain. They differ in chemical composition: as the polyoxyethylene chain gradually increases there is formed a mixture of products with various numbers of oxyethylene groups. Since the rates of the individual steps of this consecutive-parallel reaction occur at similar velocities, it follows that the content of compounds of varying degrees of oxyethylation corresponds approximately to the Poisson distribution function. A typical curve of the distribution of nonionic detergents by the number of oxyethylene groups is given in Fig. 4.11. Usually, detergents are characterized by the average number of oxyethylene groups (for example, OP-7, OP-10, stearox-6), which approximately corresponds to the maximum on the distribution curve. It should be noted that the distribution curve depends on the method of manufacture of the product: when the synthesis is carried out in a continuous back-mix reactor, the curve is more flattened than for the synthesis accomplished in a batch reactor and may have no maximum at all.

The foam-forming ability of nonionic detergents is, as a rule, lower than that of ionic detergents (alkylaryl sulphonates, for

xample) and depends on the nature of the hydrophobic portion and the length of the polyoxyethylene chain. For example, for oxyethylenated isononylphenols the maximum foam-forming ability is observed when 15-20 oxyethylene groups are introduced; an increase in the chain length or the introduction of a second alkyl group into phenol lowers its foam-forming ability. The same results are obtained by lengthening the hydrophobic portion of the molecule or other nonionics as well.

The cleansing ability of nonionic surfactants is high even without addition of phosphates or carboxymethyl cellulose. They retain cleansing properties in hard water and differ from ionics by the ability to prevent the re-deposition of dirt particles onto the fabric and by the compatibility with most of the dyes and other reagents used in the textile industry. It is because of these properties that nonionic detergents find increasing application for the laundering of various fabrics (most often in the form of mixtures with ionics), in the washing and treatment of wool, as components of cosmetics, and in the leather industry.

All nonionic cleansing compounds based on ethylene oxide are produced at 150-250 °C in the presence of bases as catalysts (about 0.3 percent NaOH or sodium methoxide) at atmospheric or elevated pressure (up to 2 MPa). The similarity in synthesis conditions is due to the fact that the step of building up of the polyoxyethylene chain is always the same: the successive addition of ethylene oxide to the alcohol groups of the primary oxyethylated product. But the step of addition of the first molecule of ethylene oxide to carboxylic acids, alkylphenols and mercaptans (and of two molecules of ethylene oxide to amines and amides) is specific for each type of the starting compound and differs from the subsequent oxyethylation steps. Also, this initial step proceeds with a different velocity (it is usually lower) and is separated from the subsequent steps in accordance with the considerations discussed above and the curves given in Fig. 4.10b.

When nonionics are to be produced from higher carboxylic acids, one essential point must be taken into account. Esters are known to be liable to undergo alcoholysis and transesterification reactions, especially upon catalysis by an alcoholate (alkoxide) formed

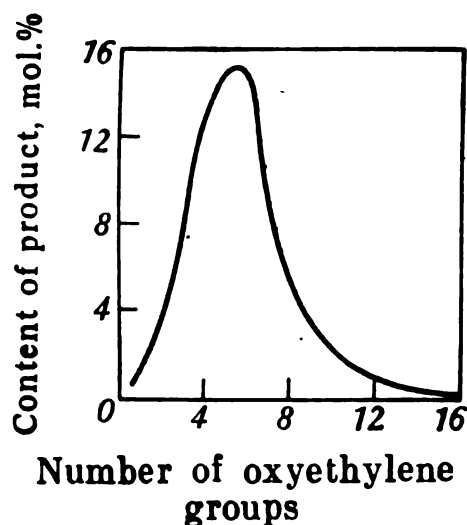
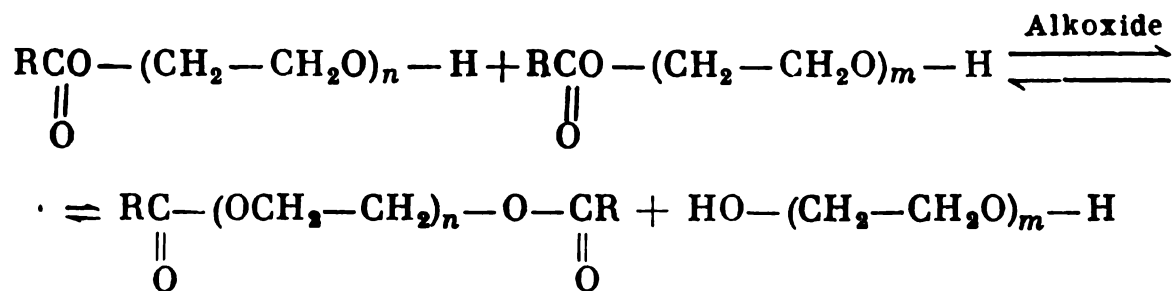


Fig. 4.11. The distribution curve for the oxyethylation of nonionic surfactants by the number of oxyethylene groups.

from alkali. As a result of this, the reaction products are an equilibrium mixture of polyglycols and their mono- and diesters:



whereas in the synthesis of other nonionic surfactants (with the exception of polymeric ones) polyglycols are formed in small amounts.

Nonionic surfactants are produced on a large industrial scale; for example, in the USA the production figures exceed 500,000 tons per year, which is about 25 percent of the total world's production of synthetic detergents (syndets).

4.4.2.2. Reaction Units

All manufacturing processes based on ethylene oxide and propylene may technologically be classified into three types.

1. Reactions accomplished with a large excess of the second reagent (i.e., with a deficiency of the α -oxide), as in the production of ethylene glycol, propylene glycol, diethylene glycols, cellosolves. The heat of the reaction is taken up by the excess reagent, as a result of which the temperature of the reaction mass increases only by 40-50 °C. This makes it possible to carry out the process under adiabatic and completely homogeneous conditions, i.e., with a preliminarily prepared solution of the α -oxide in water or alcohol. In order to maintain the reaction mass in the liquid state at 150-200 °C, a pressure of ≈ 2 MPa is required.

Such processes are carried out in continuous reaction columns with no heat-exchange surfaces (Fig. 4.12a). The starting mixture preheated by steam is fed into the top of the column and flows downwards through the central tube, in which it is heated by the reaction mass. The reaction products are taken overhead. The contact time in the production of glycols and cellosolves in the absence of catalysts is 20-30 min, this being responsible for considerable lateral mixing, which lowers the selectivity.

For such reactions to be carried out continuously but in the more intensified regime (the synthesis of glycols in the presence of phosphoric acid, the production of ethanolamines under pressure), shell-and-tube reactors are most suitable (Fig. 4.12b). The back mixing in these reactors is insignificant and the selectivity of the process is higher.

2. Reactions in which the molar ratio of the α -oxide to the other reagent is kept within the limits of 1 : (4-5) to (2-3) : 1, as in the synthesis of oxyethylated amines, thioglycols and thioesters, alkylene carbonates, etc. The amount of heat evolved is high, and if no cooling is provided, overheating of the reaction mass is inevitable. The most typical reactors used for such processes are shell-and-tube reactors with rather narrow tubes (Fig. 4.12b) or externally cooled columns (Fig. 4.12c). The shell-and-tube reactor must operate

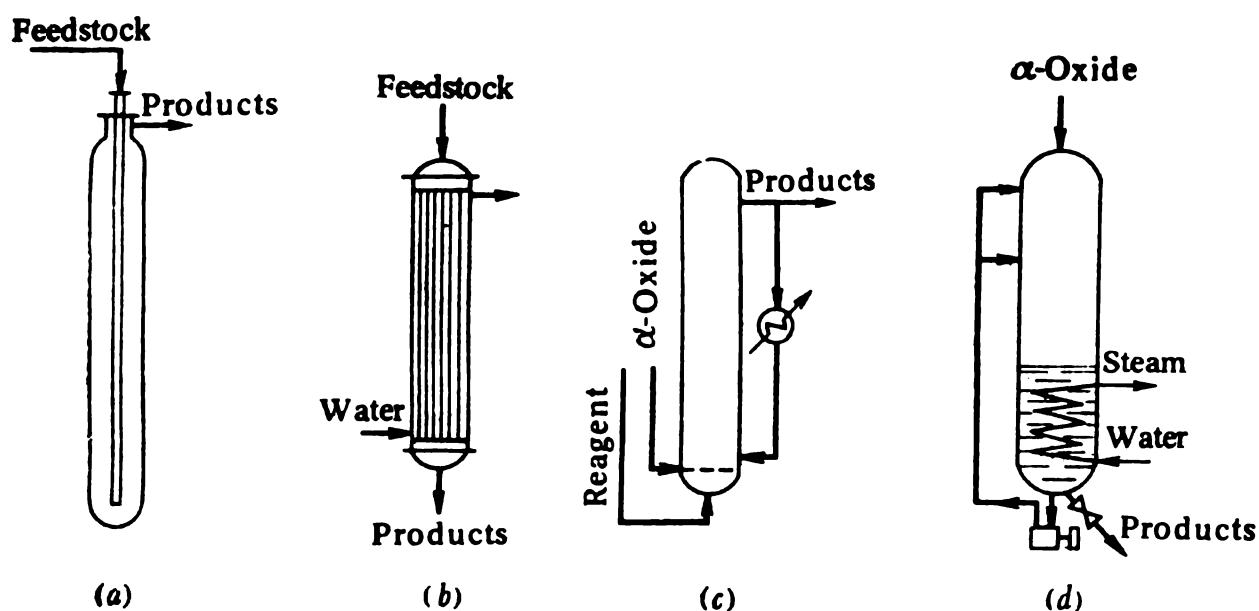


Fig. 4.12. Reaction units for oxyalkylation processes:

α —adiabatic reactor; b —shell-and-tube reactor; c —reactor with circulation of the liquid through an external cooler; d —batch apparatus with spraying of the liquid (for synthesis of nonionic surfactants).

under pressure in order to keep the reaction mixture in the liquid state. In the second reactor, intensive circulation takes place; this reactor may be employed only for those reactions in which successive conversions play no significant role (the production of alkylene carbonates, thioalcohols and thioesters). The medium here is often the reaction product, into which the gaseous reagents (ethylene oxide, and CO_2 or H_2S , etc.) are bubbled under pressure. Depending on the reaction temperature, the heat evolved is removed by water or boiling condensate; in the latter case, process steam is generated.

3. Reactions in which the molar ratio of ethylene oxide to the second reagent exceeds 3 : 1 (the synthesis of polyglycols and nonionic surfactants). In this case, the heat effect is so high that the heat removal problem assumes prime importance, especially in view of the restrictions on permissible temperatures imposed by the product quality requirements. Such processes were operated batchwise for a long period of time by bubbling the α -oxide through the liquid reaction mass, say in a batch reactor (Fig. 4.12c) or in a stirred, internally cooled reactor. Because the reaction mass becomes thickened upon successive incorporation of oxyalkyl groups into the mole-

cule the efficiency of bubbling is low, the reaction velocity is slow and the duration of the process is 8-15 hours.

In a new variant of the batch operation (Fig. 4.12d) the liquid reaction mass is dispersed in an atmosphere of gaseous α -oxide, which considerably increases the phase-contact surface and makes it possible to complete the reaction in 1.5-3 hours. The liquid in the still cooled by a suitable heat carrier (with the generation of process steam) is continually pumped through special nozzles and sprayed into the gaseous space of the reactor, into which the α -oxide is introduced, the drops being again settled into the liquid phase. The continuous operation is in the development stage.

4.4.2.3. The Flow Diagram of Production of Glycols

As an example, we shall consider the flow diagram of production of ethylene glycol (Fig. 4.13), which can be employed for the synthesis of propylene glycol. The process is carried out in the absence of catalysts at 160-200 °C under pressure to maintain the mixture in the liquid state. The mixture to be charged is prepared from fresh

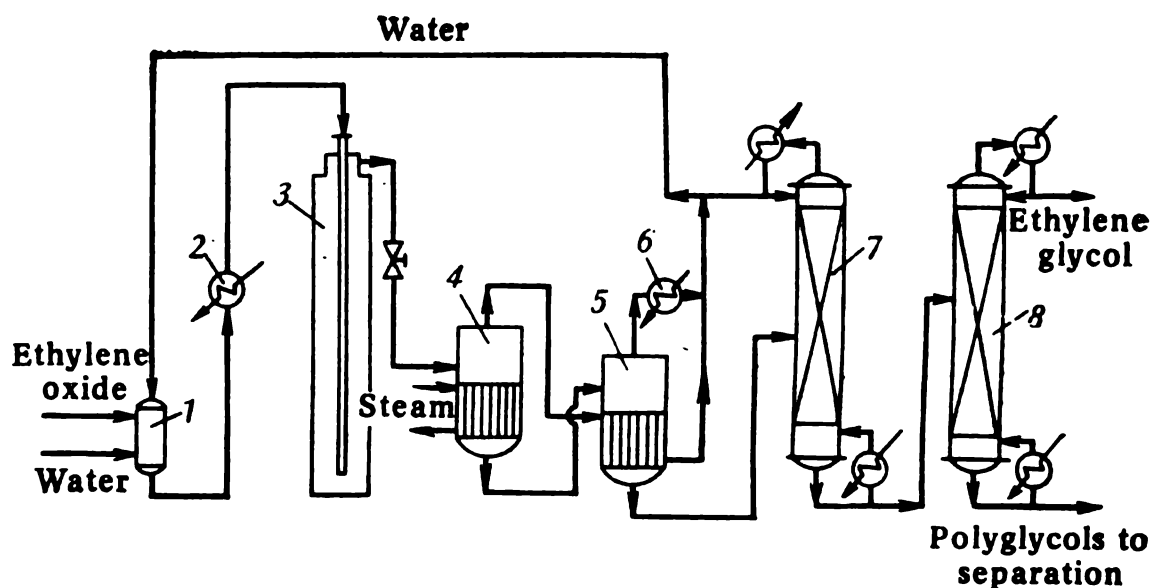


Fig. 4.13. Flow diagram of ethylene glycol production:

1—mixer; 2—steam heater; 3—reactor; 4, 5—stripping columns; 6—condenser; 7, 8—fractionating columns.

and recycle water condensates and ethylene oxide, the concentration of the oxide being 12-14 percent (by weight), which corresponds approximately to a 15-fold molar excess of water with respect to the α -oxide.

Ethylene oxide, fresh and recycle condensates are introduced under pressure into mixer 1 and then to steam heater 2, where the charge is heated up to 130-150 °C and run to reactor 3 (the reactor is of the adiabatic type described earlier). The mixture passes first through the central tube of the reactor and is additionally heated by the hot reaction mass present in the reactor space, where the

products are formed. Apart from ethylene glycol, diethylene glycol and triethylene glycol, there are formed by-products—acetaldehyde (due to the isomerization of ethylene oxide) and its condensation product. On leaving the reactor the liquid heated to 200 °C is throttled to atmospheric pressure, part of the water being evaporated and the liquid cooled down to 105-110 °C.

The mixture passes into unit 4, which is the first stage of a multi-unit stripping plant; the vacuum increases from one subsequent stage to another (up to 133 Pa); each of the subsequent stages is heated by the steam from the preceding stage [only the first (unit 4) and the last (unit 5) stages are shown in Fig. 4.13]. The still liquid leaving vessel 5 is subjected to fractionation in vacuum column 7 to separate the residual water; all the water condensates are combined and returned for the preparation of the feed and then to the reaction. The mixture of glycols from column 7 passes into vacuum column 8, where sufficiently pure ethylene glycol is distilled off, the mixture of di- and triethylene glycols being left in the still. These products are also of great value and are therefore separated in an additional vacuum-distillation unit.

In the synthesis of cellosolves the alcohol taken in excess is recirculated. Since the difference in the volatility of the alcohol and cellosolve is not too large, the mixtures are separated by fractional distillation rather than by evaporation. In the synthesis of ethanolamines, ammonia and water are recirculated and ethanolamines are separated by vacuum distillation.

In all the cases, the recirculation of large quantities of the excess reagent requires considerable expenditure of energy. If the subsequent oxyethylation products are of value by themselves, it is expedient not to produce them in special units but to carry out a combined synthesis of ethylene glycol and diethylene glycol, cellosolve and carbitol, monoethanolamine and diethanolamine with reduced excess of the second reagent.

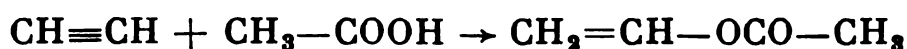
When polyglycols and nonionic surfactants are synthesized, the treatment of the reaction mass consists only of the purging of ethylene oxide and the neutralization of the alkaline catalyst by an organic acid.

4.5. Vinylation Processes

Vinylation, i.e., the introduction of the vinyl group into various compounds, can be effected by indirect and direct methods. The direct method consists of a direct interaction between various compounds and acetylene; two groups of such reactions are distinguished: (1) vinylation catalyzed by salts of transition metals (primarily, of Zn and Cu); and (2) vinylation catalyzed by alkalis.

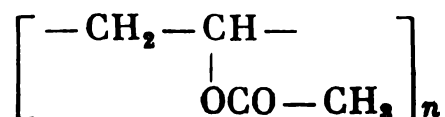
4.5.1. Vinylation Catalyzed by Transition-Metal Salts

This group of vinylation processes is closely related to the above-described hydration and hydrochlorination of acetylene leading to the formation of acetaldehyde and vinyl chloride, respectively. This process is employed industrially to produce vinyl acetate, vinylacetylene and acrylonitrile:



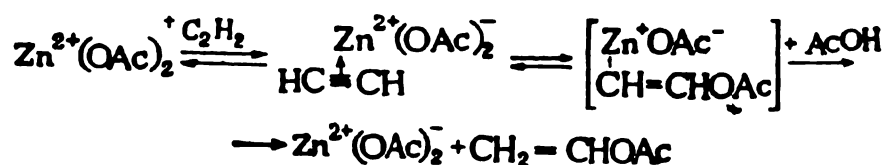
However, just as in the synthesis of acetaldehyde and vinyl chloride, there have been developed other, more economical routes for the production of the corresponding compounds from olefins in place of expensive acetylene, and the vinylation methods gradually lose their importance.

Synthesis of Vinyl Acetate. Vinyl acetate, $\text{CH}_2=\text{CH—OCO—CH}_3$, is a liquid (b.p. 72 °C), which forms explosive mixtures with air. It is one of the most important monomers and gives *polyvinyl acetate* upon polymerization:



This polymer has excellent adhesive properties and is used for the manufacture of adhesives and varnishes. The hydrolysis of polyvinyl acetate gives *polyvinyl alcohol* $[\text{—CH}_2\text{—CH(OH)—}]_n$, which is used as an emulsifying agent and a thickener for water solutions. Partly hydrolyzed polyvinyl acetate is used to produce polyvinyl acetate films and leather substitutes. Wide use is also made of copolymers of vinyl acetate with vinyl chloride and other monomers.

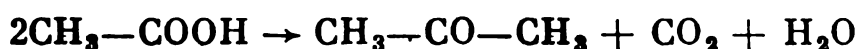
The production of vinyl acetate by the vinylation method consists of an interaction between acetylene and acetic acid. The catalyst is zinc acetate supported by activated carbon. The heterogeneous-catalytic interaction of acetylene with acetic acid is carried out in the vapour phase at 170–220 °C. The mechanism of the reaction consists of the chemisorption of acetylene with the formation of a π -complex with the zinc ion, the intracomplex attack on the activated acetylene molecule by the acetate ion and of the final reaction with acetic acid:



Vinyl acetate is capable of further addition of acetic acid with the formation of ethylene diacetate, which gives rise to a system of consecutive-parallel reactions:



The first step proceeds much faster than the second, but in order to repress the formation of ethylidene diacetate, an excess of acetylene with respect to acetic acid is required. The other by-products formed are acetaldehyde, which results from the hydrolysis of acetylene by the water present in a small amount in the reaction mass, and acetone, which results from the ketonization of the acid:



Besides, a small quantity of the compounds undergoes polymerization, forming resins. In order to avoid the extreme development of side reactions and to raise the capacity of the reactor the degree of conversion of acetic acid must not be too high (≈ 60 percent). In these conditions, the yield of vinyl acetate amounts to 95-98 percent based on acetic acid and 92-95 percent on acetylene.

The industrial synthesis of vinyl acetate employs the molar acetylene/acetic acid ratio ranging from 3.5 : 1 to 5 : 1. The catalyst is prepared by impregnation of activated charcoal with zinc acetate followed by drying. The fresh catalyst contains 30 percent of zinc acetate and is very active even at 170-180 °C. During the process it is gradually deactivated because of the deposition of the polymer and resins, which requires that the temperature be gradually raised to 210-220 °C.

The synthesis is carried out at atmospheric pressure in a tubular reactor cooled by the boiling water condensate; this generates process steam to be used at the other stages. Reactors with a fluidized catalyst bed have also been designed.

A simplified flow diagram of this process is shown in Fig. 4.14. The steam-gas mixture of the starting compounds is heated in heat exchanger 1 by the hot reaction gases and led into reactor 2. The mixture leaving reactor 2 is successively cooled in heat exchanger 1 and in a system of water and brine coolers 3, where all the liquid compounds are condensed. The unreacted acetylene is returned for the preparation of the starting mixture and the liquid is run for separation into a system of fractionating columns 5, where the light fraction, vinyl acetate, acetic acid (to be returned to the synthesis) and ethylidene diacetate are distilled off. The heavy fraction is burned.

This method is today replaced by the synthesis of vinyl acetate by way of the oxidative coupling of ethylene with acetic acid (Chapter 6).

Synthesis of Acrylonitrile and Vinylacetylene. The method of their manufacture from acetylene is based on the use of the Nieuwland catalytic system, which is one of the first metal-complex catalysts. It is a concentrated (35-40 percent) aqueous solution of Cu_2Cl_2 and NH_4Cl , to which NaCl or KCl acidified up to $\text{pH} = 1-5$ is added.

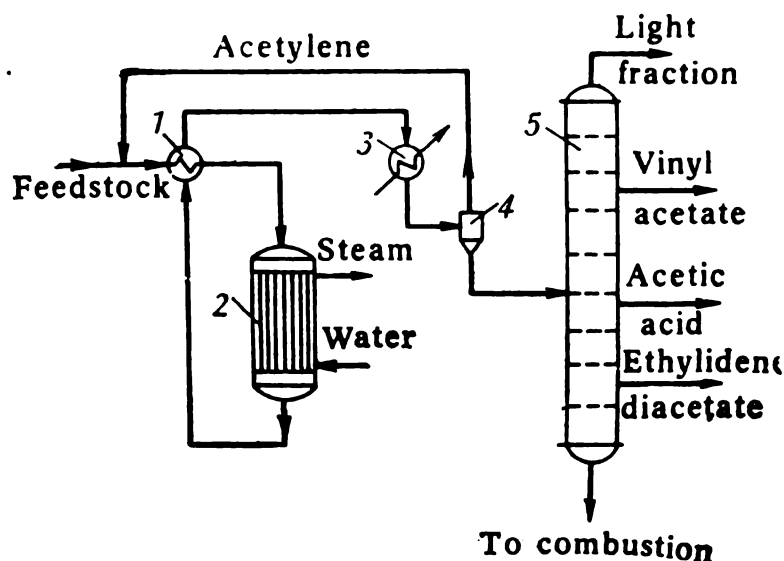
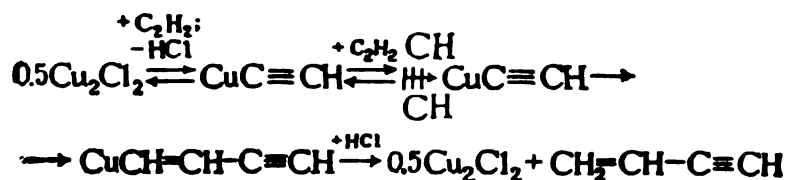
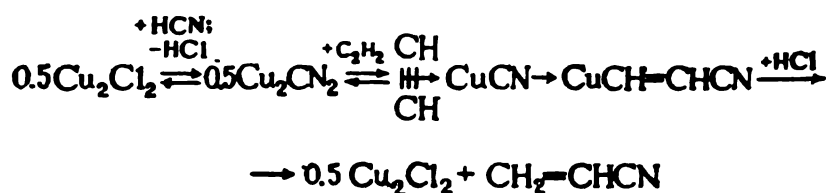


Fig. 4.14. Flow diagram for synthesis of vinyl acetate from acetylene:

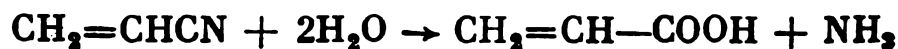
1—heat exchanger; 2—reactor; 3—cooler-condenser; 4—separator; 5—fractionation unit.

In this system there are formed associated cuprammonium complexes capable of forming coordination complexes with acetylene and of ligand exchange. The syntheses using this catalyst are believed to proceed by the insertion mechanism:



The two reactions are accompanied by successive conversions—the formation of acetylene trimer and polymers in the synthesis of vinylacetylene:

$2\text{C}_2\text{H}_2 \rightarrow \text{CH}_2=\text{CH}-\text{C}\equiv\text{CH} \xrightarrow{+\text{C}_2\text{H}_2} \text{CH}_2=\text{C}-\text{C}-\text{CH}=\text{CH}_2$ and so on
and by the hydrolysis of acrylonitrile:



and by the formation of other products. Therefore, it is important to blow off the end products from the catalyst solution by the excess acetylene bubbled through the solution; the acetylene is then returned

to the reaction. That is why both processes are carried out in bubbler columns protected from corrosion by acid-resistant sheets; acetylene or a mixture of acetylene and hydrocyanic acid bubbles through the catalyst solution. The heat evolved in the reaction is removed by heating the reagents and evaporating the products.

Vinylacetylene is of value for the production of chloroprene (chlorobutadiene), a monomer for synthetic rubber, but today this method of chloroprene synthesis is replaced by another process based on the use of cheaper butadiene (page 186).

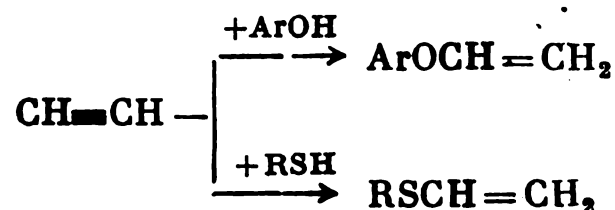
Acrylonitrile is one of the most important monomers, whose properties and uses and the method of its manufacture from propylene will be described in Chapter 6.

4.5.2. Vinylation Catalyzed by Alkalis

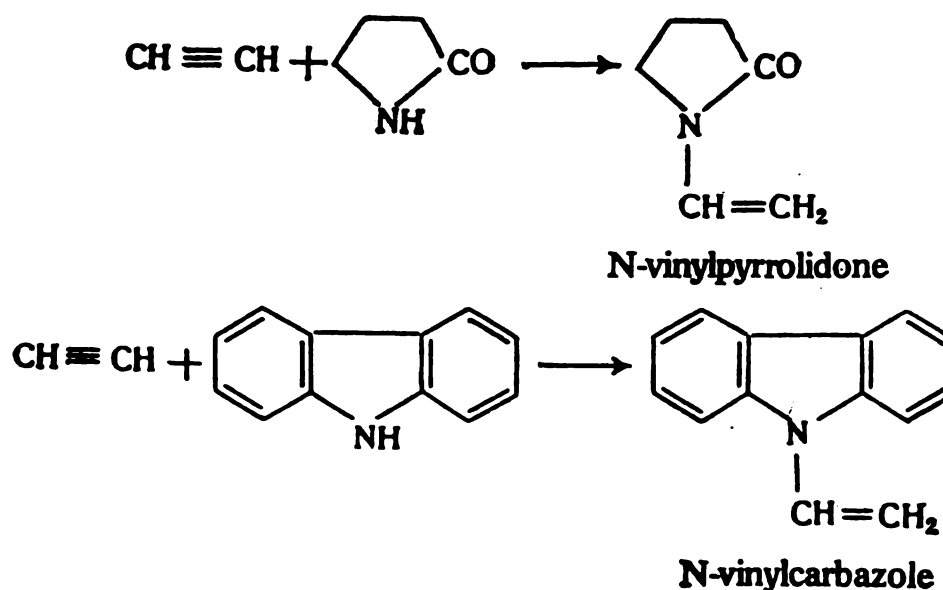
The vinylation of alcohols in the presence of alkalis, which was discovered by A. E. Favorsky, is a very convenient route for the synthesis of vinyl ethers:



Apart from alcohols, phenols and mercaptans are also capable of entering into an analogous reaction in the presence of alkalis:

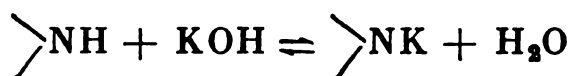


The vinylation by acetylene may also proceed at the nitrogen atom in amines or amides having weak acidic properties due to the conjugation of the amino group with the neighbouring unsaturated bonds or aromatic systems, just as, for example, in α -pyrrolidone or carbazole:

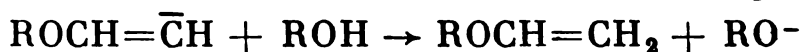


The reactivity of alcohols in vinylation reactions decreases with their increasing acidity. Therefore, of the saturated monohydric alcohols, methanol reacts with the slowest rate; for methanol to be vinylated one has to maintain the temperature within the range of 160-170 °C (the temperature required for higher alcohols is 130-140 °C). With phenol even more severe conditions (up to 200 °C) are required.

The catalysts that may be used for the reaction of acetylene with alcohols are alcoholates (alkoxides); for reactions with phenol use is made of phenolates (phenoxides), etc. Best results are obtained with potassium hydroxide, which reacts with an organic reagent exhibiting acidic properties to give a metallic derivative:



whose anion is a strong base. The mechanism of the subsequent reaction consists of the nucleophilic addition across the acetylene linkage; the process starts with the attack of the anion and ends with a proton exchange, as a result of which the anion is regenerated:



The rate of the process depends on the nucleophilic activity of the reagents, which accounts for the above-indicated relationship between reactivity and structure.

Vinyl ethers obtained from acetylene and alcohols are of practical industrial value chiefly as monomers for the synthesis of polymeric compounds. They are polymerized by an ionic mechanism under the action of mineral acids or metal halides. The polymers formed may be viscous liquids, solids or rubber-like compounds, this being dependent on the nature of the ether and the molecular mass of the polymer. The polymers are noted for excellent cementing and strong adhesion to various surfaces. This accounts for their use in adhesives, varnishes, etc.

Most vinyl ethers are colourless liquids. Two examples are *vinyl ethyl ether*, $\text{C}_2\text{H}_5\text{—O—CH=CH}_2$ (b.p. 37 °C) and *vinyl isobutyl ether*, $(\text{CH}_3)_3\text{C—O—CH=CH}_2$ (b.p. 81 °C).

Of great practical value are N-vinylated nitrogen compounds produced from acetylene and the corresponding amine or amide in the presence of an alkali. For instance, *N-vinylpyrrolidone* is polymerized to yield *polyvinylpyrrolidone*, which is used in medicine as a blood plasma expander and in the cosmetics industry as a dispersing agent and a thickener.

N-Vinylcarbazole (a crystalline compound; m.p. 67 °C) gives *polyvinyl carbazole* on polymerization. It has excellent mechanical

strength and dielectric properties and good thermal stability. It is used as a heat-resistant dielectric (as a substitute for mica or asbestos) in electrical equipment and as an insulator in television and radio sets.

Technology of Alkaline Vinylation. All the vinylation reactions considered above are carried out only in the liquid phase with acetylene being bubbled through the reaction mass containing 10-20 percent KOH dissolved in the reagent. Because of the high temperature, only reactions with higher alcohols or, in general, with high-boiling compounds may be effected at a pressure close to atmospheric. For the vinylation of lower alcohols a pressure of 0.5 to 2-2.5 MPa is required in order to keep the reaction mass in the liquid state.

Besides, the increased pressure of acetylene contributes to the acceleration of the reaction, which is why the vinylation of high-boiling compounds is also sometimes carried out at elevated pressure (for example, the synthesis of N-vinylcarbazole).

Because of the explosive properties of acetylene, in processes carried out under pressure it is diluted with nitrogen so as to exclude explosion hazard. For example, when vinyl isobutyl ether is to be produced (at ≈ 0.5 MPa) acetylene is diluted with 35 percent (by volume) of nitrogen; in the synthesis of vinyl methyl ether (≈ 2.5 MPa) 55 percent (by volume) of nitrogen is required. For reactions carried out under pressure close to atmospheric use may be made of concentrated acetylene. It is most useful to dilute acetylene with the vapours of the reagent itself if it is sufficiently volatile at the reaction temperature.

The reaction vessel in all cases is a hollow bubbler column. Acetylene (plus nitrogen) is fed into the bottom of the column and bubbled through the liquid reaction mass. The unabsorbed acetylene is taken overhead and is returned by means of a circulation compressor to the reaction after it is separated from the volatile compounds entrained by it. The heat is removed chiefly by the evaporation of a certain amount of the reaction mixture, whose vapours are condensed in a reflux condenser, the condensate being returned to the reactor. This makes it possible to simplify the reactor design and to maintain the autothermal regime in the reactor.

When the vinyl ether to be synthesized is more volatile than the reagent (which is the case with lower alcohols), it is continually taken off from the reaction unit together with the residual acetylene, is isolated by condensation or absorption and purified from the entrained alcohol by fractional distillation. In the synthesis of high-boiling compounds (say N-vinylcarbazole) special heat-exchange units are provided to remove the heat. The reaction products left in the liquid reaction mass and is isolated from it by an operation dependent on the properties of the components. The production of N-vinylcarbazole employs a hydrocarbon solvent—methyl-

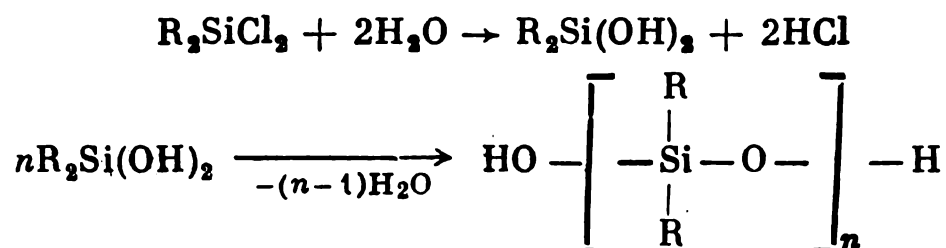
or dimethylcyclohexane, which is added to the carbazole in an amount of 100 percent (by weight). It dissolves N-vinylcarbazole and extracts it from the reaction mass, thus preventing further conversions under the action of alkali and acetylene. The solvent is then distilled off and sufficiently pure N-vinylcarbazole is obtained after vacuum fractionation.

4.6. Alkylation at Atoms of Other Elements

Alkylation at atoms of silicon, aluminium and other elements is the principal route for the synthesis of the simplest organoelement and organometallic compounds, from which a wide range of their derivatives are obtained by various methods. The chemistry and technology of organoelement compounds are highly specific and their production is the concern of special branches of industry. Therefore, in this chapter we shall consider only those principal products which are within the scope of the industry of organic and petrochemical synthesis by the scale of production and commercial value.

4.6.1. Synthesis of Organosilicon Compounds

The chemistry and technology of organosilicon compounds have developed vigorously for the last 20-30 years. The impetus to their development was the industrial importance of many of these compounds, notably organosilicon polymers, lubricating oils and liquids noted for their high thermal stability, this being due to the presence of the strong siloxane linkage Si—O—Si. The starting materials for the production of these organosilicon compounds are dialkyl- or alkylaryldichlorosilanes, R_2SiCl_2 . The reaction of these compounds with water gives silanediols, which undergo condensation with the formation of linear polymers:



4.6.1.1. Direct Synthesis of Organochlorosilanes

Organosilicon compounds were obtained for a long period of time by the following method of organomagnesium synthesis:

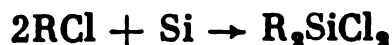


These methods could not find extensive application in the industry until Rochow discovered in 1945 the direct synthesis of alkylchloro-

rosilanes, which marked the beginning of the vigorous development of the production of organosilicon compounds.

The direct synthesis of organochlorosilanes is based on the reaction of chloro derivatives with metallic silicon or better with the catalyst mass containing not only silicon but copper as well. Addition of copper makes it possible to lower the reaction temperature and to avoid the development of pyrolytic processes, which reduce the yield of the end products. Apart from copper, other metals (aluminium, zinc, silver) have also been tested for this purpose, but the silicon-copper catalyst has proved to be the least expensive and most efficient. It is prepared by fusion of silicon with copper, by sintering their powders in a hydrogen atmosphere or by chemical deposition of copper onto silicon. The catalyst usually contains 80-95 percent of silicon and 5-20 percent of copper.

When alkyl chlorides react with metallic silicon in the presence of copper at 300-450 °C, Si-alkylation occurs, which leads to the formation of a complex mixture of products. The major product is dialkyldichlorosilane



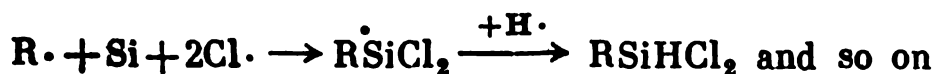
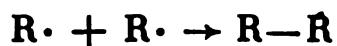
There are also formed monoalkyltrichlorosilanes (RSiCl_3), trialkylmonochlorosilanes (R_3SiCl), silicon tetrachloride (SiCl_4), chlorosilane hydrides (RSiHCl_2 , R_2SiHCl) and also decomposition products—hydrogen, methane, ethylene, ethane, etc. These reactions proceed by a free-radical mechanism. It is believed that the primary act is the interaction of an alkyl chloride with copper, which gives copper alkylate or alkylcopper chloride, these being then decomposed with the formation of free hydrocarbon radicals and chlorine atoms:



The free atoms and radicals then react with a silicon atom, forming alkylchlorosilanes:



By-products are formed as a result of the dimerization of the free radicals and atoms and also of the dehydrogenation of the hydrocarbons and the interaction of the intermediates with hydrogen:



The tendency to react directly with a silicon-copper catalyst is exhibited mainly by the simplest alkyl chlorides (methyl and ethyl chlorides), allyl chloride and chlorobenzene. The higher chloroalkanes are strongly decomposed, and vinyl chloride gives a low yield of the end product because of its low reactivity. With methyl and ethyl chlorides the reaction occurs at 300-370 °C, but for the reaction with chlorobenzene to be accomplished the temperature must be raised to 430-470 and even to 500-600 °C.

The degree of conversion and the yield of the end product depend not only on the temperature but also on the reaction time, the degree of pulverization of the silicon-copper catalyst, the promoters

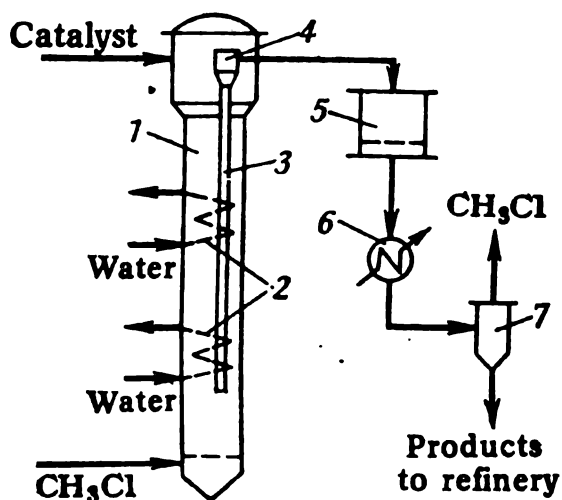


Fig. 4.15. Reaction unit for direct synthesis of alkylchlorosilanes:

1—reactor; 2—cooling pipes; 3—pipe for particles of copper-silicon catalyst; 4—cyclone; 5—filter; 6—cooler-condenser; 7—separator.

added to the catalyst, no local overheatings, the stirring intensity, the presence of foreign gases, etc. For example, when the reaction mass is diluted with nitrogen (25-50 percent), a better temperature control is possible and the yield of dimethyldichlorosilane increases. When the catalyst mass is stirred, the degree of conversion of chloro derivatives increases and the composition of the product is improved. Many of the factors indicated have probably an indirect effect, thus facilitating the temperature control.

Two variants of industrial process apparatus are employed. In one of them, use is made of horizontal revolving reactors: chloro derivatives are fed from one side and reaction products removed from the other. The catalyst mass to be regenerated moves countercurrently to the reaction gases. The heat of the reaction is removed either by diluting the chloro derivative with nitrogen or by cooling means. The degree of conversion of the chloro derivative in such a reactor exceeds 90 percent.

In the second method, the process is operated in a reactor with a fluidized silicon-copper catalyst bed (Fig. 4.15). The reactor is a vertical tube, into the lower section of which methyl chloride is introduced. The gas stream keeps the tiny particles of the catalyst mass in a fluidized state, this providing good mixing. For the temperature in the reaction space to be controlled, water is circulating through tubes 2. In the upper, flared section of the reaction unit the solid particles are separated from the gaseous reaction products. These products are additionally purified from the smallest particles in cyclone 4 and filter 5, cooled and condensed. The resultant con-

densate is sent for further processing. In such reactors, the degree of conversion of alkyl chlorides is lower than in tubular reactors, amounting only to 60 percent, which is why the unreacted methyl chloride (the gas left after the condensate is separated) is recycled to the reaction.

The method of direct synthesis is most important for the production of methylchlorosilanes. The major end product is *dimethyldichlorosilane*, $(\text{CH}_3)_2\text{SiCl}_2$, but the yield of the product is only 50-60 percent; the by-product formed is *methyltrichlorosilane*, CH_3SiCl_3 (10-20 percent). Dimethyldichlorosilane is a colourless liquid (b.p. 70°C), which fumes in air. It is the major feedstock for the synthesis of polysiloxanes (silicones). Methyltrichlorosilane boils at 65°C . The other by-products also have close boiling points and have therefore to be separated by multistage fractionation.

The mixture formed in the reaction of ethyl chloride with a silicon-copper catalyst consists of 35-40 percent $(\text{C}_2\text{H}_5)_2\text{SiCl}_2$, 20-30 percent $\text{C}_2\text{H}_5\text{SiCl}_3$, 10-15 percent $\text{C}_2\text{H}_5\text{SiHCl}_2$ and smaller quantities of other compounds. The end product *dichlorodiethylsilane*, $(\text{C}_2\text{H}_5)_2\text{SiCl}_2$, boils at 129°C . In this particular case the difference in vapour pressure of the various products is large enough for the products to be successfully separated by fractionation.

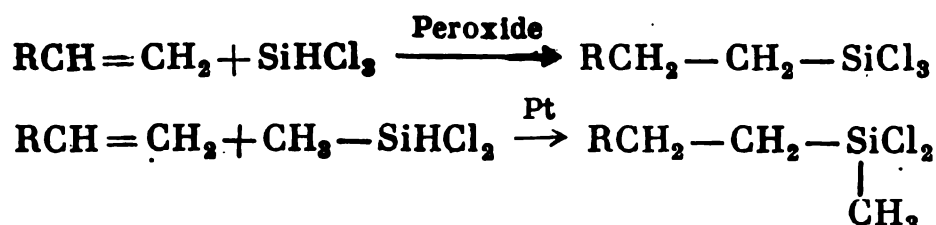
In the reaction of an ordinary silicon-copper catalyst with chlorobenzene the degree of conversion is low; it is therefore recommended that the copper content in the catalyst be raised up to 30 percent. The reaction products consist mainly of *phenyltrichlorosilane*, $\text{C}_6\text{H}_5\text{SiCl}_3$; the content of *diphenyldichlorosilane*, $(\text{C}_6\text{H}_5)_2\text{SiCl}_2$, is lower.

4.6.1.2. Other Alkylation Reaction at the Silicon Atom

The direct synthesis of alkylchlorosilanes gives good results only for a limited number of compounds (methyl-, ethyl- and allylchlorosilanes). Therefore, other industrial methods have been developed for the production of other organosilicon compounds. The most important of these reactions are alkylations at the silicon atom (or the silylation of organic compounds).

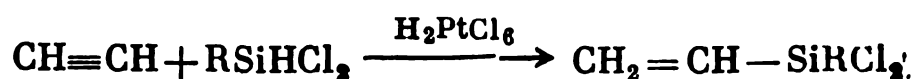
The starting silicon-containing compounds for these processes are chlorosilane hydrides, SiHCl_3 , produced from hydrogen chloride over a silicon-copper catalyst, and especially chlorosilane alkylhydrides, RSiHCl_2 , which are formed as by-products in the direct synthesis. It has been found that the hydrogen atoms attached to silicon are capable of being replaced by various alkyl groups under the action of the corresponding alkylating (and arylating) agents. One type of reaction is the interaction of olefins with hydridechlorosilanes and alkylhydridechlorosilanes, which proceeds under the action of peroxides and ultraviolet radiation and also in the

presence of aluminium, boron or zinc halides and platinum-based catalysts (supported platinum or platinohydrochloric acid, H_2PtCl_6):



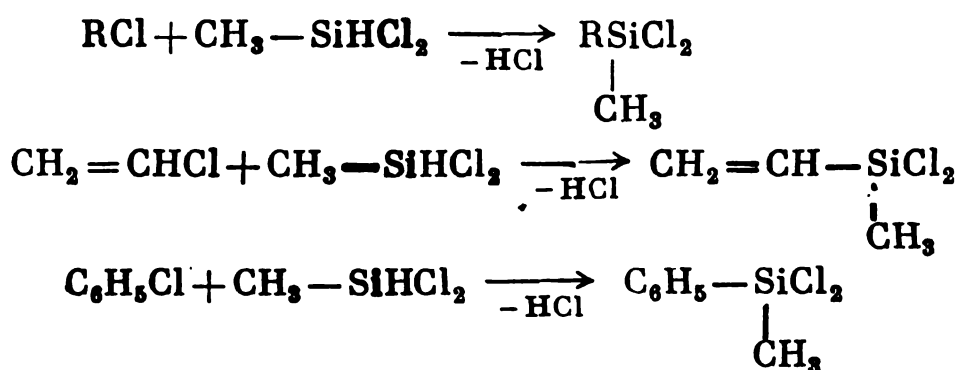
The addition of hydridechlorosilanes occurs so that the silicon-containing group is directed to the more hydrogenated carbon atom.

Acetylene reacts with hydridechlorosilanes and alkylhydridechlorosilanes in the same way as olefins, the vinylation taking place at the silicon atom:



This route is employed to obtain vinyl organosilicon compounds, the direct synthesis of which gives unsatisfactory results.

The hydrogen atom linked to silicon can also be replaced upon interaction with chloro derivatives. The reaction proceeds most efficiently at high temperature (600-700 °C), but for a number of syntheses the use of the catalysts mentioned above has been recommended. Not only chloroalkanes but also unsaturated aromatic chloro derivatives can enter into this reaction:



Thus, by combining the direct synthesis with the above-described condensation of hydridechlorosilanes and alkylhydridechlorosilanes with unsaturated hydrocarbons and chloro derivatives it is possible to obtain numerous organosilicon compounds containing, in particular, aromatic rings and unsaturated bonds or mixed dialkyl- and alkylarylchlorosilanes, such as, for example, *dichloromethylphenylsilane*, $\text{CH}_3(\text{C}_6\text{H}_5)\text{SiCl}_2$.

4.6.2. Organoaluminium Compounds and Syntheses Based on Them

Organoaluminium compounds have become important for the last 20 years as catalysts for stereoregular polymerization of olefins

and as intermediates of organic synthesis. They are used for the production of α -olefins and primary alcohols with a straight chain of carbon atoms, which are especially suitable for the synthesis of biodegradable surfactants.

4.6.2.1. Synthesis of Organoaluminium Compounds

Organoaluminium compounds were first obtained from chloro derivatives by organomagnesium synthesis. Alkyl chlorides are still used today for the production of so-called ethyl aluminium sesquichlorides, which are formed from ethyl chloride and activated aluminium powder in an inert solvent:



Another method of their manufacture consists of the disproportionation of anhydrous aluminium chloride with triethyl aluminium at 50-60 °C in gasoline:



Diethylaluminium chloride is a colourless liquid (b.p. 65-66 °C at ≈ 1.6 kPa). Like other organoaluminium compounds, it spontaneously ignites in air and is decomposed by water. It is the main component of Ziegler-Natta catalysts used for the polymerization of olefins that also contain TiCl_4 or other metal chlorides.

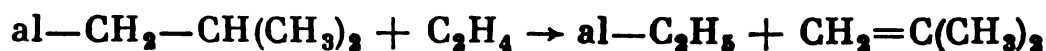
The direct synthesis of alkylaluminium from aluminium and olefins was discovered by Ziegler in 1955. The reaction occurs most simply with isobutylene, which at 140-150 °C and 4-6 MPa in gasoline gives triisobutylaluminium:



In contrast to isobutylene, the reaction with ethylene carried out under the same conditions leads to a considerable development of the *side reaction of building-up of the alkyl chain*, which is characteristic of organoaluminium compounds:



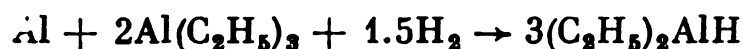
In this connection, a two-step process has been proposed for the production of triethylaluminium, which consists of the preliminary synthesis of triisobutylaluminium and its subsequent interaction with ethylene:



This *reaction of displacement of alkyl groups* is typical of organo-aluminium compounds and proceeds at elevated temperature or in the presence of catalysts.

Wider use is made of another method of production of triethylaluminium, in which triisobutylaluminium is not synthesized, but there is recycle of triethylaluminium. This method also consists of two steps.

The first step is the interaction of aluminium with recycle triethylaluminium and hydrogen leading to diethylaluminium hydride:



The reaction proceeds at 100-140 °C and 2-5 MPa. In the second step, diethylaluminium hydride reacts with ethylene under mild conditions (60-70 °C, \approx 2 MPa), when there is practically no build-up of the chain:

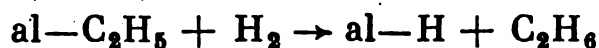


Thus, per each mole of the newly formed triethylaluminium there are circulating 2 moles of the product, this being an essential drawback of the two-step process. A one-step process has also been proposed for the synthesis but it involves the recirculation of triethylaluminium as well.

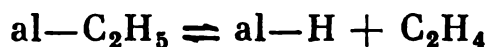
An important condition for the successful realization of all these heterogeneous processes is the high degree of dispersion of aluminium and activation of its surface for removal of the oxide film with the aid of chemical reagents (ethyl bromide, triethylaluminium, AlCl_3) or by grinding in mills. Besides, it has been observed that with very pure aluminium the reaction does not proceed, while the presence of impurities of transition metals (Ti and others) substantially accelerates the process. Therefore, use is made of aluminium doped with 0.8-4 percent of titanium or else titanium hydride is added as catalyst. The rôle of titanium hydride is probably to donate hydrogen to aluminium atoms, whose hydrides are capable of direct interaction with olefins. Addition of trialkylaluminiums probably favours the formation of dimer complexes with titanium hydrides and radicals, which involve metallic aluminium into subsequent conversions.

The synthesis and processing of alkylaluminiums may involve a number of reactions leading to the formation of by-products. Upon ethylation there is obtained a small quantity of diethylbutylaluminium due to the lengthening of the chain. An oxygen impurity in the gases is responsible for the presence of aluminium alkoxides, say $\text{Al}(\text{OR})_3$, in the products. Hydrogen is capable of hydro-

generating alkylaluminiums, giving paraffins:



Alkylaluminiums themselves can undergo reversible decomposition at elevated temperature:



a fact that has to be taken into account in their distillation, which is carried out in the atmosphere of the corresponding olefin.

Triethylaluminium (a liquid; b.p. 128-130 °C at 6.65 kPa) and *triisobutylaluminium* (a liquid; b.p. 138 °C at 0.66 kPa) are highly reactive compounds. They react vigorously with water and spontaneously ignite in air. All the operations involving these compounds must be carried out in the atmosphere of dry oxygen-free nitrogen.

Process Technology. The synthesis of triethylaluminium is carried out batchwise or continuously, the main operations in both cases being the activation of aluminium, the preparation of the

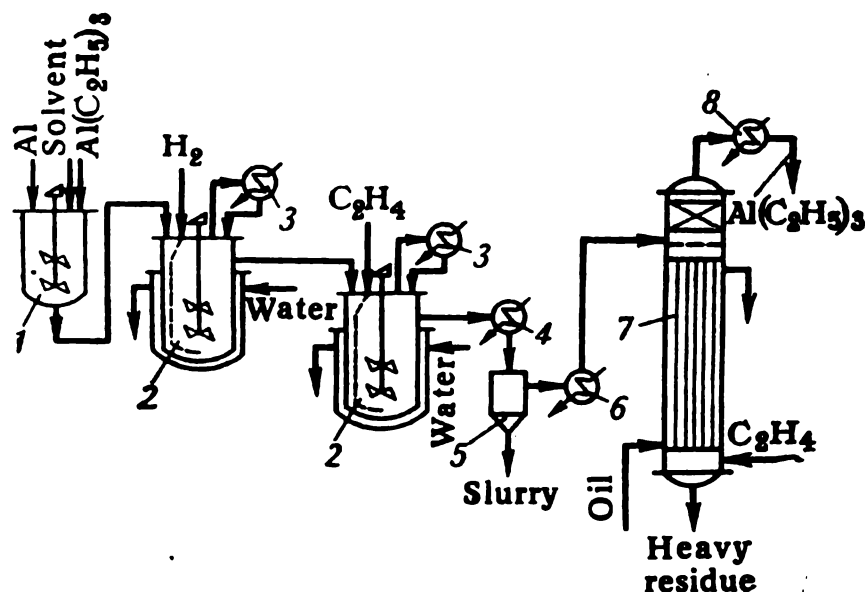


Fig. 4.16. Flow diagram for production of triethylaluminium:

1—mixer; 2—reactors; 3—reflux condensers; 4—cooler; 5—centrifuge; 6—steam preheater; 7—film vaporizer; 8—condenser.

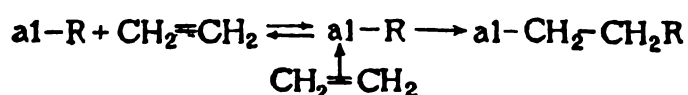
charge, the synthesis of the end product, the separation of unreacted aluminium, and distillation by which the end product is isolated.

A simplified flow diagram of the process is presented in Fig. 4.16. The charge is prepared in mixer 1, into which aluminium powder, solvent (gasoline, heptane or toluene) and recycle triethylaluminium are introduced. Before charging the mixer is blown off with nitrogen (the other units are also blown off), which is also used to accomplish the transport of the streams. From the mixer (several mixers are required for the continuous process) the resultant suspension is led to a cascade of stirred jacketed reactors 2 equipped with reflux condensers 3.

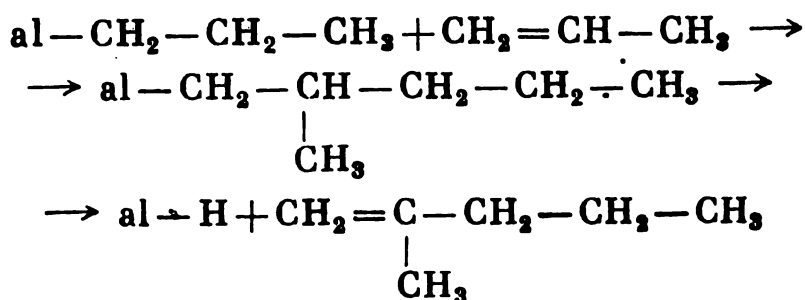
Hydrogen is supplied under pressure into the first reactor, where diethylaluminium hydride is synthesized; this compound is then transferred to the second reactor where it is converted into triethylaluminium under the action of ethylene (also under pressure). The reaction mass from each of the reactors overflows into the next reactor through the side pipe. On leaving the last reactor the reaction mass is chilled in cooler 4 and separated from the aluminium sludge in centrifuge 5, where the sludge is washed with the solvent and then mixed with the oil and burned. The liquid leaving the centrifuge is separated from residual sludge and less volatile by-products by distillation; the distillation is effected in the atmosphere of ethylene in film vaporizer 7 heated by oil in order to avoid the decomposition of the product (the film distillation makes it possible to reduce the residence time of the compounds at high temperatures and to prevent overheating). The vapours are chilled in cooler 8, the condensate is separated from ethylene (then returned to distillation) and the liquid is separated into two streams: part of it is recycled to the step of preparation of the feed and the remainder is withdrawn as the final product.

4.6.2.2. Production of Linear α -Olefins

We have already described the method of production of linear α -olefins by the thermal cracking of paraffin (page 49). Another synthetic route of their manufacture involves the oligomerization of ethylene using organoaluminium compounds. It is based on the above-mentioned reactions of organoaluminium compounds: the buildup and displacement of alkyl groups. The first reaction is the insertion of an olefin molecule across the Al—C bond into trialkylaluminium via the intermediate formation of a donor-acceptor complex:

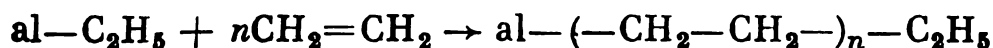


With ethylene homologues the insertion occurs so that the aluminium atom becomes linked to the most hydrogenated carbon atom. It is because of this that the reaction between tripropylaluminium and propylene leads eventually to 2-methyl-1-pentene:



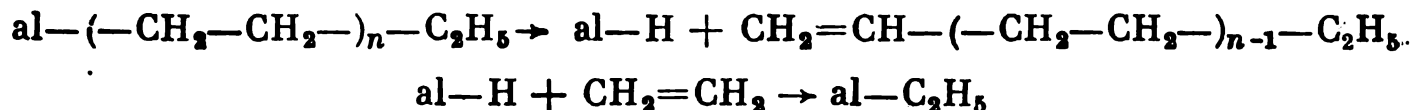
This reaction forms the basis of the methods of isoprene production (see Chapter 6).

The sequential buildup of alkyl groups occurs statistically; as a result, triethylaluminium and ethylene give alkylaluminiums of differing chain length, the chain having a linear structure and containing an even number of carbon atoms:



Here the content of alkyl groups of differing chain length corresponds to the Poisson distribution, which has already been encountered (see Fig. 4.11). As a result, the product with an average degree of oligomerization (≈ 7), which is most suited for the synthesis of α -olefins (to be used for the manufacture of surfactants), contains a considerable number of C_4 - C_{10} and $\geq \text{C}_{20}$ olefins. The average degree of oligomerization is controlled during the reaction of buildup of the chain by changing the molar ratio of the converted ethylene to the trialkylaluminium taken.

The second reaction (the displacement of alkyl groups) consists of the initial splitting of alkylaluminiums into an olefin and aluminium hydride; the latter is then reacted with the olefin, which is used to effect the displacement:



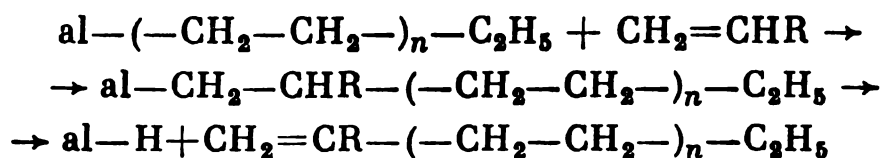
This reaction has a higher activation energy than the chain-buildup reaction and is effected at a higher temperature or in the presence of catalysts (dispersed or supported nickel).

The separate realization of the reactions of building-up and displacement of alkyl groups forms the basis of the *two-step process* of organoaluminium synthesis of α -olefins. Triethyl aluminium and ethylene are charged into the chain-buildup reactor maintained at a temperature of 100-130 °C and a pressure of 9 MPa. The resulting product is sent to the displacement reactor, where triethylaluminium is recovered and α -olefins are formed in the atmosphere of ethylene. This process is effected thermally (at 200-300 °C) or catalytically in the presence of nickel (dispersed or supported nickel). A shortcoming of the process is the recycle of a large quantity of triethylaluminium—1 mole per 3 moles of the α -olefin produced.

The *one-step synthesis* of α -olefins is based on the combination of the buildup and displacement reactions, which is achieved at ≈ 200 °C, when their rates become comparable. In this case, up to 250 moles of α -olefins can be formed per 1 mole of triethylaluminium and, hence, triethylaluminium may be taken in catalytic amounts and its regeneration may even be omitted.

The product obtained also consists of a mixture of olefins of differing chain length and its composition corresponds to the Poisson distribution law. However, the average degree of oligomerization depends in this particular case on the ratio of the rates of the buildup and displacement reactions. For example, when the temperature is increased and the ethylene pressure reduced (i.e., when its concentration in the liquid phase decreases), the average degree of oligomerization falls off and vice versa.

The combination of buildup and displacement reactions leads to the formation of by-product branched olefins as a result of the participation of gradually accumulated α -olefins as well as ethylene in the chain buildup reaction:



In order to repress this side reaction, an excess of ethylene is required, which is why the process is carried out at 15-28 MPa and the degree of conversion of ethylene is limited to 60-75 percent. The yield of branched olefins also decreases when the high-temperature

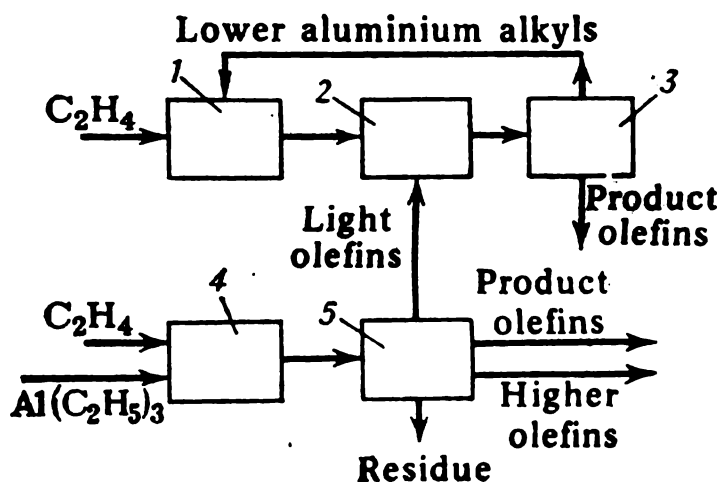


Fig. 4.17. Flow diagram of the modified process of ethylene oligomerization: 1—chain buildup unit; 2—displacement unit; 3—separation unit; 4—high-temperature oligomerization unit; 5—separation unit.

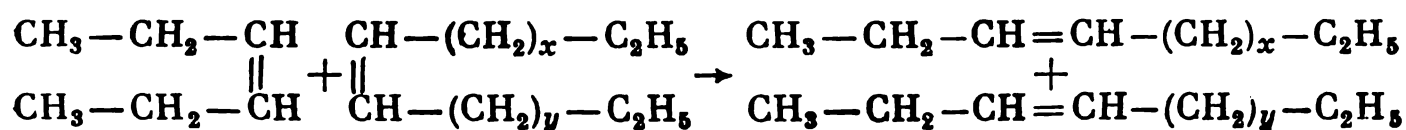
oligomerization is effected in a reactor approaching in design the plug-flow model, this being satisfied most completely by tubular reactors cooled by a boiling water condensate.

All the measures indicated above allow the yield of linear olefins to be increased to ≈ 95 percent, but the end C_{12} - C_{18} fraction suitable for the synthesis of surfactants is produced in a yield of 40-50 percent; with account taken of the C_8 - C_{10} fraction the yield is only 60-70 percent.

In this connection, modified processes have appeared for the oligomerization of ethylene aimed at synthesizing narrower fractions of α -olefins. The flow diagram of one of these modified processes is given in Fig. 4.17.

The high-temperature oligomerization of ethylene is carried out in reactor unit 4, where a mixture of α -olefins and alkylaluminiums is obtained; this mixture is separated in unit 5 into the end, light and heavy (higher) olefinic fractions; the residue consists of the products of decomposition of alkylaluminiums. The light olefins are run to unit 2, where they displace the end olefins from the alkylaluminiums obtained in unit 1. The end olefins are separated in unit 3 from lower alkylaluminiums and sent to chain buildup unit 1, where the chain of the lower alkylaluminiums is lengthened by the action of ethylene to the desired length. The resultant alkylaluminiums exchange alkyl groups with the light olefins in displacement unit 2; an additional amount of the end fraction is isolated in unit 3. In this process only the higher olefins ($> C_{20}$) are of little value and the yield of the end fraction increases up to 80 percent.

The new modified process makes it possible to process both light and heavy α -olefins into the end fraction. After the high-temperature oligomerization products are separated the mixture is subjected to catalytic isomerization, which leads to the migration of double bonds into the carbon chain. This is followed by the disproportionation of the mixture of olefins resulting in the formation of compounds having a medium chain length:

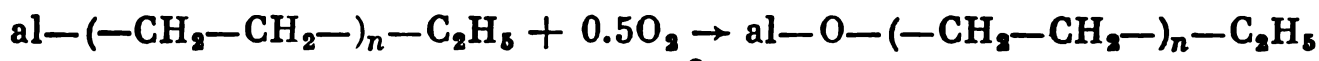


The resultant olefins are finally again subjected to isomerization, but this time the reaction proceeds with the migration of the double bond to the end positions. As a result, the yield of the end fraction of α -olefins (C_{12} - C_{18}) increases even more. It should be noted that the last isomerization step is not obligatory, since for some fields of application of olefins the position of the double bond in their molecule is not important because of its displacement in subsequent reactions (in the alkylation of benzene for the production of surfactants of the type of alkylphenyl sulphonates).

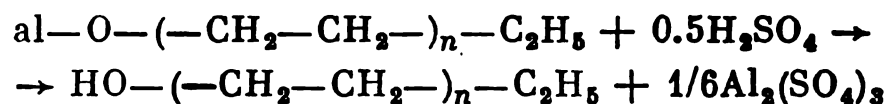
4.6.2.3. Synthesis of Linear Primary Alcohols

The organoaluminium synthesis of higher primary alcohols of linear structure involves the above-considered steps of production of triethylaluminium and higher alkylaluminiums. The latter are

oxidized by air to give aluminium alkoxides:



and the alkoxides are hydrolyzed by sulphuric acid to obtain a mixture of primary alcohols having a linear structure:



A simplified flow diagram of the *Alfol process* is shown in Fig. 4.18. The chain-buildup step is effected in a coil reactor 1, into which triethylaluminium (mixed with a solvent) and ethylene are fed at a pressure of 8-10 MPa. In order to avoid the formation of olefins (because of the displacement reactions), the temperature is strictly kept within the range of 120-130 °C, the coils being cooled by using a suitable coolant. The reaction mass is throttled to a low pressure and the liquid phase is separated in separator 2 from the unreacted ethylene.

The alkylaluminiums are then sent together with the solvent to a bubbler column 3 for oxidation; air is admitted to this column, the heat of the reaction being removed by the evaporation of the solvent. Its vapours are condensed in cooler 4 and the condensate is recycled to the reactor. The effluent gases containing only a small amount of

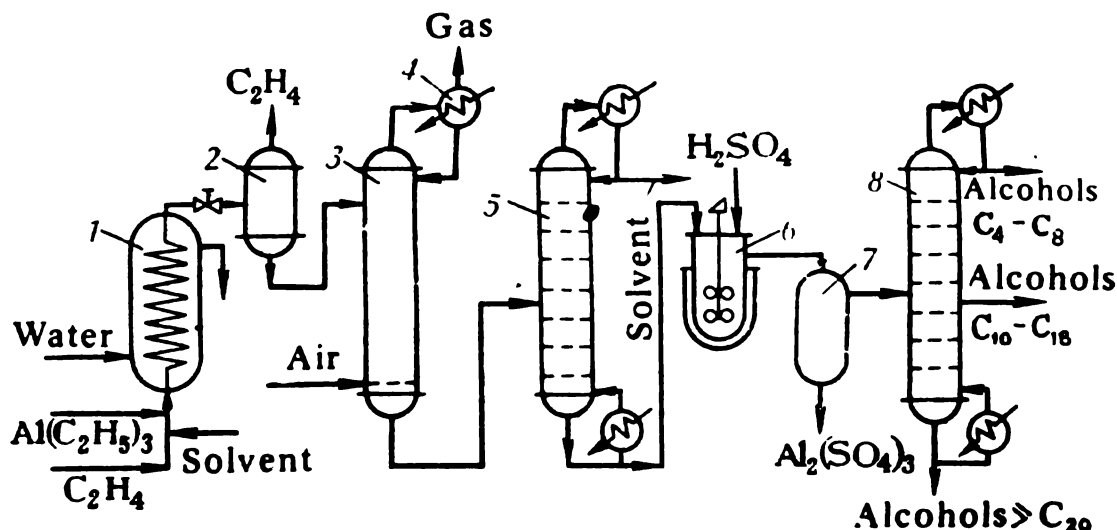


Fig. 4.18. Flow diagram of the Alfol process for production of primary alcohols
1—reactor; 2—separator; 3—oxidation column; 4—reflux condenser; 5—solvent distillation column; 6—hydrolyzer; 7—alums separation unit; 8—fractionating column.

unconverted oxygen are withdrawn for recovery of the solvent vapours or for burning. The resultant aluminium alkoxides pass from the still of column 3 to column 5, where the solvent is distilled off, and then to stirred unit 6 for hydrolysis.

The hydrolysis is carried out using concentrated sulphuric acid on cooling: the mild reaction conditions are developed by using a continuous back-mix reactor. The resultant mass is transferred for separation; first, the aluminium sulphate (alums) is separated and then the alcohols are fractionated to derive products having different chain lengths.

This method of synthesis of primary alcohols has been realized on an industrial scale in a number of countries and competes with the other methods of their production to be described further in the text.

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